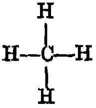
NOTES OF TEN INTRODUCTORY LECTURES
ON
ORGANIC CHEMISTRY
WITH SPECIAL REFERENCE TO
COAL

Organic Chemistry may be defined as that branch of chemistry which deals with the compounds of carbon.

The subject is a very great one, and this may best be understood when it is realised that there are well over one million organic or carbon compounds.

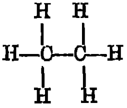
The mother element is carbon ; in itself, carbon is an inert substance, and does not react readily. It occurs in three distinct types (*i e.*, three distinct and different modifications) namely, diamond, graphite (crystalline), and charcoal (non-crystalline). In the two former modifications, carbon is in a state of very great purity.

In organic compounds, carbon is always tetravalent, *i.e.*, it has four affinities with which it may combine with other elements. This question of the affinities of an element is a characteristic of the element. Hydrogen is monovalent, oxygen divalent, chlorine bromine and iodine monovalent. In other words, carbon may combine with four atoms of hydrogen or two atoms of oxygen ; the following shows the constitution formulæ of methane, ethane, and carbon dioxide :—



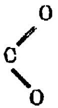
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Methane.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane.



Carbon Dioxide

Carbon possesses the property in a very high degree of combining with itself, thus producing compounds of very great complexity, which may contain a large number of carbon atoms in a molecule.

The simplest organic compound is —

Methane (CH_4), Fire Damp or Marsh Gas

This compound is a gas, and is the mother substance of the series of compounds called the saturated hydrocarbons or paraffins The second member of this group is ethane (C_2H_6) and the third propane (C_3H_8), which are always found associated with naturally occurring methane.

An examination of the formulæ of these compounds shows that one member differs from the next higher member by a CH_2 group, and the increment is constant. Such a series of compounds is called a homologous series, and one member is said to be a homologue of the simplest member of the series. Thus, ethane and propane are homologues of methane.

The following table shows the chief members of the series of saturated hydrocarbons —

PARAFFINS —C_nH_{2n+2}.

Formula	Name.	Melting Point.	Boiling Point.	Specific Gravity.	
CH_4	Methane	—186°	—164°	·415 at b.p.	
C_2H_6	Ethane	—172°	—90°	·446	at 0°
C_3H_8	Propane		—38°	·536	
C_4H_{10}	Normal Butane		+ 1°	·600	
	Isobutane		—17°		
C_5H_{12}	Normal Pentane		+36°	·633	at 15°
	Dimethylethylmethane or Isopenthane		+28°	·627	
	Tetramethylmethane or Neopentane		+10°		
C_6H_{14}	Normal Hexane		69°	·677	at 0°
	Dimethylisopropylmethane		58°	·679	
	Dimethylpropylmethane		62°	·672	
	Methyldiethylmethane		64°		
	Trimethylethylmethane		48°		
C_7H_{16}	Heptane		98°	·700	at 0°
	Isoheptane		98°	·697	
C_8H_{18}	Octane		125°	·718	
C_9H_{20}	Nonane		150°	·733	
$C_{10}H_{22}$	Decane		173°	·745	

ormula.	Name.	Melting Point.	Boiling Point.		Specific Gravity.	
$_{11}H_{24}$	Undecane		195°		·774	At the Melting Point.
$_{12}H_{26}$	Dodecane		214°		·773	
$_{13}H_{28}$	Tridecane		234°		·775	
$_{14}H_{30}$	Tetradecane		252°		·775	
$_{15}H_{32}$	Pentadecane		270°		·776	
$_{16}H_{34}$	Hexadecane	18°	287°		·775	
$_{17}H_{36}$	Heptadecane	22°	303°		·777	
$_{18}H_{38}$	Octadecane	28°	317°		·777	
$_{19}H_{40}$	Nonadecane	32°	330°		777	
$_{20}H_{42}$	Eicosane	37°	205°	At 15 mm. pressure	·778	
$_{21}H_{44}$	Heneicosane	40°	215°		·778	
$_{22}H_{46}$	Docosane	44°	224°		·778	
$_{23}H_{48}$	Tricosane	48°	234°		·779	
$_{24}H_{50}$	Tetracosane	51°	243°		·779	
$_{27}H_{56}$	Heptacosane	60°	270°		·780	
$_{31}H_{64}$	Hentriacontane	68°	302°		·781	
$_{32}H_{66}$	Dotriacontane	70°	310°		·781	
$_{35}H_{72}$	Pentatriacontane	75°	331°		·782	

The formulæ for such a series may be written in general terms, and that for the methane series or paraffins is C_nH_{2n+2} where " n " represents the number of carbon atoms in the compound. The general term paraffins is used owing to the compounds being very inert chemically (parum affinis = little affinity).

The properties of the members of such a series of compounds undergo a gradual change as the number of carbon atoms in the compounds increase. Thus, the boiling point, melting point, viscosity (or fluidity), specific gravity, flash point, and calorific value all increase as the number of carbon atoms increase. Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are gases at the ordinary temperature. Commencing with butane (C_4H_{10}), the boiling point of which is 1° C., the compounds are liquids, and when hexadecane ($C_{16}H_{34}$) is reached all are semi-solids or solids at the ordinary temperature.

The whole of the members of this series are contained both in American and to some extent Russian petroleum. The compounds are separated by fractional distillation, and when the boiling point becomes excessively high, the distillation is, in some cases, carried out under vacuum, hence the term " Vacuum Oils." The distillates are briefly as follows: petroleum ether, petrol, ligroin, kerosine, paraffin (or burning) oil, lubricating oil, vaseline, paraffin wax, and, finally, petroleum pitch or petroleum charcoal.

The approximate boiling points of the commercial fractions of petroleum are:—

	°C.
Petroleum Ether (or petrol)	36 to 90
Ligroin	90 to 120
Benzoline or Benzine (*not* Benzene)	120 to 150
Paraffin Oil or Burning Oil or Kerosene	150 to 250
Gas Oil or Solar Oil	200 to 300
Lubricating Oils	200 to 300
Vaseline or Petroleum Jelly	—
Paraffin Wax	M.P. 45 to 65

Commercial petrol varies in boiling point and properties according to the demands of the market; generally the former is between 60°C. and 140°C., and its specific gravity 0·700 to 0·740. It will be seen, therefore, that it is a mixture of a number of the members of this series and its properties depend upon which are present.

The gaseous members of the series may be obtained from the decomposition of coal, but they can hardly be considered to be present in coal in its natural state. Thus, coal gas contains about 32 per cent. of a mixture of methane, ethane, and propane; the percentage of ethane being about 5.

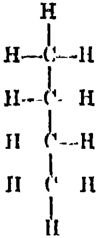
The gaseous and liquid members of the series are obtained by the distillation of coal or cannel at a low temperature (low temperature carbonisation) and the production of the series is one of the chief objects aimed at by the low temperature carbonisation of coal and other fuels. The series is quite distinct from the compounds obtained by the high temperature distillation of coal.

Methane is also produced by the decomposition of organic matter by bacteria, stagnant water, ponds; it is interesting to note that at certain sewage farms and elsewhere, light and heat are obtained by burning sewer gas (methane, 97 per cent.).

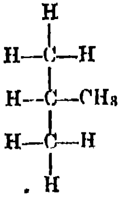
Another source of this series should be mentioned: namely, by the distillation of shale, an industry which flourishes in Scotland.

Isomerism.

In the more complicated hydrocarbons, beginning with butane (C_4H_{10}) two or more arrangements of the atoms present in the compound are possible. Thus, butane may be written —



Butane.
BP+1°C



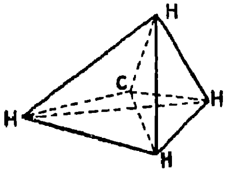
Iso-Butane
B.P−17°C

It will be noticed that the compounds have the same empirical formula, but possess different physical and chemical properties. One compound is said to be an isomer of the other, that is to say, a blood brother.

Pentane (C_5H_{12}) has three isomers. Hexane (C_6H_{14}) has five isomers. Tridecane ($C_{13}H_{28}$), however, has 802 isomers. The three isomers of pentane are called primary (B.P. + 36), secondary (B.P. 28°C.), and tertiary or neopentane (B.P. 10°C.). It is clear that the distillates from petroleum which are obtained by distillation at certain temperatures will be complicated mixtures of different isomers ; further that fractions obtained from separate sources may contain entirely different compounds, although the boiling points and specific gravities of each may be the same. In other words, the fractions may be identical when tested by physical tests, but may behave differently when undergoing chemical reactions, *e.g.*, exploding in a cylinder for power production.

The Writing of Formulæ.

The method of writing the formulæ of compounds, as shown hitherto, is not sound, as it only indicates the grouping of the atoms in two dimensions—length and breadth ; it is desirable to show the formula in three dimensions—length, breadth, and depth, in order to represent matter. To indicate the four valencies or forces with which other elements become associated in the case of a carbon atom, it is necessary to assume that the valencies are equally distributed around the central carbon atom. The conception of the carbon atom is, therefore, best indicated by assuming that it is the centre of a tetrahedron, and that the valencies are effective towards the points of the tetrahedron. Methane, therefore, is written as follows :—



The modern conception of an atom is that it consists of a central nucleus or nuclei, surrounded by a sphere of influence which is composed of ions revolving round the nucleus These ions carry electrical charges, the sum of which is equal and opposite to that of the nucleus or nuclei.

In view of the above arrangement of the valencies of the carbon atom, when a chain of carbons is formed, it is not straight, and tends to form a ring. Under certain conditions, this actually happens owing to the ring compounds being more stable than the original chain compounds. Thus, pentane (C_5H_{12}) may become (C_5H_{10}) pentamethylene.

The Burning of Gases.

When methane is mixed with an excess of air or oxygen, or the theoretical volume of air, it forms an explosive mixture. If this mixture is ignited, the following equation represents the reaction which occurs.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

The explosion which takes place cannot be considered a fierce one, as there is only an increase in volume of the gases. Pressures as high as 100lbs. on the square inch have been recorded, and since the gases produced by the explosion contain a large proportion of steam, the subsequent cooling of the gases leads to the production of a diminished pressure or vacuum. The explosive limits of methane in air are between 6 and 16 per cent. ; mixtures containing more or less than these limits are non-explosive. The reaction between the two gases may be brought about by means of a catalytic agent or catalyst. In such a reaction the catalyst which brings it about is not altered. When a mixture of methane and air is exploded, it means that the compound has undergone a very rapid oxidation, but it has been proved that this reaction really takes place atom by atom.

Stage I. of the oxidation of methane.

$$CH_4 + O = CH_3OH.$$

Methyl Alcohol.

It will be noticed that in the compound methyl alcohol the group (CH_3—) is combined with the group (OH) Such groups, which possess the power of passing from one compound to another and still retain their original formula and characteristic properties, are called radicles. Radicles may be monovalent (*e.g.*, methyl (CH_3—), ethyl (C_2H_5—), propyl (C_3H_7—), hydroxyl (OH)), or di- or trivalent, &c.

Methyl Alcohol (CH_3OH) may therefore be called methyl hydrate or methyl hydroxide or hydroxymethane. Commercially it is called wood spirit or methyl alcohol.

Stage II. of the oxidation of methane.

$CH_3OH + O = H_2O + HCHO$ or Formaldehyde.

Stage III. of the oxidation of methane.

$HCHO + O = HCOOH$ or Formic Acid.

Stage IV. of the oxidation of methane.

$HCOOH + O = CO_2 + H_2O.$

The final result of the above four stages is as follows :—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

When methane is burned in a limited quantity of air, the chief product obtained is carbon monoxide.

It will be seen from the above that the oxidation of methane is a gradual process, and this may be said of all other chemical reactions. Such reactions proceed more or less rapidly, but always step by step. Therefore, an explosion is simply combustion taking place very rapidly.

Experiments on the above problem were carried out by Dr. Coward, who mixed air with methane, the mixtures being made of such a dilution that they were not explosive (below 5 per cent. of methane); the mixed gases were brought into a box 7 ft. long by 1 ft. square with two glass sides, and containing an arrangement at the bottom by which a single electrical spark could be produced at will. When a spark was made in the mixture a vortex ring of flame was produced, starting at the sparking point. The ring of flame travelled upwards, enlarging as it rose, until it reached the upper end of the box, where it was extinguished. The ring of flame was found to ignite explosive mixtures, and it would appear from these experiments that a flame will travel through a gaseous mixture which in itself is not explosive, and may reach an explosive mixture when an explosion would occur. The ignition temperature for different gases varies with the amount of air or oxygen added.

	Mixed with oxygen.	Mixed with air.
Hydrogen ignites at ..	.. about 580° C.	580° C.
Carbon monoxide	.. ,, 650	650
Methane	.. from 558 to 700	650 to 750

Carbon Monoxide (CO) ("After-damp").

This gas is colourless and tasteless, except when in high concentrations, when it produces a taste similar to that of metallic copper. In this compound carbon is divalent, but it must be assumed that two of the valencies are inactive.

Carbon monoxide is produced when any organic compound is burned in insufficient oxygen or air. Thus, it is formed during the burning of coal, methane and coal gas, and other fuel gases. It is the active constituent of all producer gases (about 25 per cent.), water gas (about 40 per cent.), and is present in coal gas (about 7 per cent.).

Producer gas is made by passing air through red hot charcoal, coke, coal, or other fuel, and when made from pure carbon contains theoretically 34·5 per cent. of carbon monoxide and 65·5 per cent. of nitrogen. Such a gas has a calorific value of about 110 British Thermal Units per cubic foot. (Coal gas has a calorific value of about 500 B.T.U. per cubic foot). The calorific value of pure carbon monoxide is 340 B.T.U per cubic foot, whilst methane is 1,064 B.T.U. per cubic foot.

Carbon monoxide is absorbed by the blood, producing a pink coloration, and this reaction is used as a characteristic test for carbon monoxide. The actual colour produced is a very vivid pink, which is very distinctive. Acetylene also produces a pink colour, but not of the same shade as that given by carbon monoxide.

Test for Carbon Monoxide.

A drop of freshly drawn blood is diluted with pure water until the volume is about two tablespoonsful. The liquid, which possesses a buff colour and not a red one, is divided into two equal parts. One portion is placed in a test tube and corked up to be used as a check tube to match the result of the test The other tube is exposed to the gas to be examined. The gas should be drawn through the tube, and the contents well shaken. The colour of the liquid should now be compared with that in the check tube.

Carbon monoxide is a cumulative poison ; 0·5 per cent. by volume in the air will kill a human being outright ; whilst 0·1 per cent. to 0·2 per cent. will act after a certain number of hours. Even smaller percentages (0·01 to 0·1 per cent.) have a poisonous action upon the human being, and it appears to depend upon the general health of the subject and the life led by him as to whether the poisonous effect will appear rapidly or after an extended period. The poisonous effect may not appear as a direct poisoning, but produces anæmia and other similar disturbances. A consideration of the above and an appreciation of the fact that in order to obtain high efficiency in the burning of fuel gases it is necessary to burn the gas in as small a volume of air as possible, will make it clear that gas poisoning may be a very frequent occurrence industrially. If the flame of burning gas is cooled before the combustion has completed itself, then carbon monoxide will pass into the air and be a source of danger. This may also be brought about by an insufficient supply of air, and thus, in the case of gas fires, any dull part or any part of the flames which comes in contact with cool surfaces may cause carbon monoxide to be evolved.

Amongst the number of processes liable to carbon monoxide poisoning the following may be mentioned · gas producers, gas engines, or near imperfect gas fires ; in laundries from gas irons, collar-ironing machinery ; near coke fires ; from ordinary gas ovens and burners ; blastfurnaces, and in coal mines. It is generally stated that 80 to 90 per cent of the deaths which occur in explosions in coal mines are due to carbon monoxide poisoning. " After damp " may contain from 2 to 10 per cent. of carbon monoxide. It is clear that it is a deadly poison.

The Combustion of Carbon.

In the combustion of carbon in, say, a coke or coal fire, the old theory was that at the bottom of the fire carbon dioxide was formed, and as this passed up through the fire that it took up carbon from the red-hot fuel and produced carbon monoxide This gas then passed to the top of the bed of fuel and there came in contact with an additional supply of air, and burned to produce carbon dioxide. The above theory has been replaced by one in which it is assumed that carbon monoxide and carbon dioxide are both formed together and the proportion of each formed is dependent upon the temperature of the carbon and the volume of air present. The carbon dioxide produced may, as it passes through the red-hot fuel, be reduced to carbon monoxide (the term " reduced " in chemistry means roughly that the proportion of oxygen in the compound is lowered ; thus CO_2 by taking up another carbon atom becomes 2 of CO).

$$CO_2 + C = 2CO$$

Carbon Dioxide. (CO_2.)

This is also called " black damp " and is produced by the complete combustion of carbon in air. Normal air contains 0·04 per cent. of carbon dioxide. (Air contains 21 per cent. of oxygen, 78 per cent. of nitrogen, and 1 per cent. of argon, there are also present minute quantities of sulphur dioxide and nitrogen oxide, ammonia, &c.). The accumulation of carbon dioxide in the air is prevented by the action of plant life, carbon dioxide being absorbed by the presence of sunlight, and oxygen evolved during the process.

During the complete combustion of carbon, 14,646 B.T.U's. are evolved for every pound of carbon burned, whereas by the burning of carbon to carbon monoxide only 4,383 B.T U's. are evolved.

It appears somewhat strange that one atom of oxygen, combining with carbon to yield carbon monoxide, should evolve 4,383 B.T.U's., while two atoms of oxygens to the same weight of carbon yield 14,646 B.T.U's. It would appear that the first atom of oxygen produces far less visible heat than the second. This is explained by the fact that heat is required to transform the solid carbon into gaseous form

A chemical equation does not represent fully what occurs when two or more elements of compounds interact, and in order to make the expression complete it is necessary to introduce the amount of heat gained or lost during the chemical reaction. Thus,

For unity $C + O = CO + 4{,}383$ B T.U.
1 vol. 2 vols.

For unity · $C + O_2 = CO_2 + 14{,}646$ B.T.U.
2 vols. 2 vols.

The above are called Thermal Equations.

The above equations also show that when carbon combines with oxygen, it yields either carbon monoxide or carbon dioxide, as the case may be, but that the volume of gas produced for the combustion of one unit of carbon is exactly the same in both cases. This is explained by the fact that a molecule of gas is produced, and that the volume occupied by a molecule of all gases is the same. The theory that underlies this is one evolved by Avogardo. This states that equal volumes of all gases contain an equal number of molecules. Obviously the weight of the molecules will differ and thus the weight of carbon monoxide produced from one atom or twelve units of carbon is 28, whereas the weight of carbon dioxide produced is 44.

Unsaturated Hydrocarbons.

In addition to the methane series there are other series of hydrocarbons of considerable importance from the point of view of gaseous and liquid fuels, and two of the most important of the series are the ethylene series of unsaturated hydrocarbons and the acetylene series

The first member of the first mentioned series is ethylene (C_2H_4) which is a colourless gas with a faint and rather pleasant odour. It is produced during the carbonisation or dry distillation of all organic compounds including coal. It is present in coal gas to the extent of 4 per cent., and is responsible for about one-third of the luminosity of coal gas, the remaining two-thirds being due to the presence of benzene, toluene, &c. The series of which ethylene is the first member have the general formula C_nH_{2n}, and they are most active from a chemical point of view.

The first four members are: ethylene, propylene, amylene, hexylene. These hydrocarbons possess similar physical properties to those of the saturated hydrocarbons, and the boiling points, specific gravities, &c, of the members of the two classes are generally close together for members containing the same number of carbon atoms. The unsaturated hydrocarbons occur in the products obtained during the carbonisation of coal at low temperatures. The tar and oils obtained during the carbonisation of coal tend to contain a higher proportion of these hydrocarbons the lower the temperature at which the carbonisation of the coal was carried out. The hydrocarbons are also present in certain types of petroleum, and are quite as valuable as the members of the saturated series of hydrocarbons for use as motor fuels. One fuel recently examined was found to contain butylene 16 per cent., amylene 14 per cent, hexylene, &c., 70 per cent. The subject has received very little attention up to the present, but with the increased demand for liquid fuels will no doubt be thoroughly investigated.

The first and most important member of the acetylene series is acetylene (C_2H_2).

It is produced by the action of water upon calcium carbide and is formed during the carbonisation of organic compounds. It is present in coal gas to the extent of up to 0·7 per cent. It yields copper and silver compounds called acetylides. These compounds are highly explosive. Acetylene is a colourless gas which, when pure, is practically odourless, but in the impure state possesses a disagreeable odour It is extremely poisonous but to a less degree than carbon monoxide. Its action on the human system is similar to that of carbon monoxide.

Calorific Value of Gases present in Gaseous Fuels.

	B.T.U. per cubic foot.	
	Gross.	Net.
Hydrogen	343·3	287·2
Carbon Monoxide	340·4	340·4
Methane	1064·0	951·3
Ethane.	1860·0	1691·0
Ethylene	1673·0	1561·0
Propylene	2474·0	2305·0

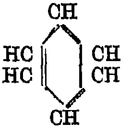
The Benzene Series.

This series of compounds is derived from a mother substance called benzene or, commercially, benzol. The whole series is called the Aromatic Series, as certain of the better known compounds have an aromatic odour.

Benzene may be produced by passing acetylene through a red hot tube or by bringing it into contact with red-hot surfaces. Therefore, if acetylene or ethylene are produced during the decomposition of coal or other fuel, and the resulting gases come in contact with red-hot coke or the surfaces of the retort then the molecules combine together and give rise to benzene and its homologues.

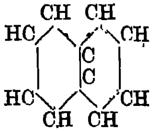
$$3C_2H_2 = C_6H_6.$$

The combination of three acetylene groups as shown above is called Polymerisation. The formula for benzene is written in the following manner, and it will be seen that it is in the form of a ring or nucleus.

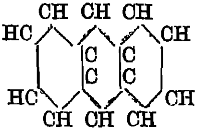


When acetylene and ethylene are heated to a higher temperature the following compounds are produced in addition to benzene —

Naphthalene.



Anthracene

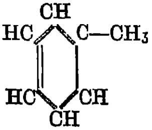


Speaking in general terms, the higher the temperature to which organic compounds are heated, the more complicated the compounds formed. Therefore, ordinary coal tar consists of an extremely complicated mixture of compounds.

The following table shows the approximate composition of coal tar produced by high temperature carbonisation :—

	Per cent.
Benzene and its homologues ..	1 4
Naphthalene and its homologues ..	4·0
Creosote Oil (a complicated mixture which is not usually separated) .	24·0
Anthracene	0·2
Water	15·0
Carbolic Acid	0·2
Pitch	55·0

Benzene (C_6H_6) is the simplest member or mother substance of a series of compounds which can be considered as derived from benzene in exactly the same manner as ethane, propane, &c., are derived from methane. Thus, benzene (C_6H_6) yields toluene or toluol ($C_6H_5CH_3$). All the hydrogens in the benzene ring may be replaced.



Toluene.

Properties of Benzene.

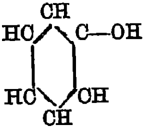
Pure benzene or benzol is a colourless liquid, having a characteristic odour. It melts at 5·4°C, and boils at 80·5° C, and has a specific gravity of 0·874.

It is clear, therefore, that if benzene is cooled to the freezing point of water it will become solid, and this is a distinct disadvantage when using benzol for motive purposes.

Toluene, the second homologue of the series, boils at 110° C., and does not become solid until —98° C. It follows, therefore, that benzene which contains a small proportion of toluene will not solidify so readily as pure benzene. On this account, it is better to use such a mixture as 90's benzol.

Commercial benzene or benzol is frequently sold under such designations as 90 per cent. or 90's benzol, or 50 per cent. or 50's benzol. Such samples contain mixtures of benzene, toluene and xylene and small percentages of higher homologues. The sample is valued by determining the volume of the liquid which will distil below 100° C. Ninety per cent. or 90's benzol means that 90 per cent. of it will distil over below 100° C. A typical sample contained benzene 85 per cent., toluene 11 per cent., xylene 1·5 per cent., and 2·5 per cent. of a mixture of unsaturated hydrocarbons, thiophene, carbon disulphide, &c.

Amongst the most important compounds in coal tar is phenol or carbolic acid, which may be considered as phenyl hydrate. This compound is the beginning of a new series of compounds :—



The compounds mentioned above are all separated from coal tar produced by the high temperature carbonisation of coal Briefly the process by which they are separated is as follows :—

The coal tar is subjected to a rough or preliminary distillation.

The first fraction is the oil which distils over below 170° C., and is called Light Oil because it has a specific gravity less than water. This oil contains benzene, toluene, xylene, and other compounds

Benzene boiling point	80° C.
Toluene ,, ...	110° C.
Xylenes ,, ...	139° C.

The second fraction is collected between 170° C., and 230° C., and is called Middle Oil. It contains naphthalene (boiling point 218° C.) and its homologues, and carbolic acid (boiling point 183° C.) and its homologues.

The third fraction is collected between 230° and 270° C., and as its specific gravity is greater than water, it is called Heavy Oil. This fraction is not usually separated, and is sold under a number of names, but may be called Creosote.

The fourth fraction is collected between 270° C. until no further compounds will distil. This is usually at a temperature of 420° C. It is called Anthracene Oil, and is the source from which anthracene is obtained.

Remaining in the retort after the above distillation is Coal Tar Pitch, the degree of hardness of which depends upon the temperature to which it has been heated. The higher the temperature the harder the pitch.

Each of the above fractions now undergoes further distillation or chemical treatment in order to recover the constituents present. In an ordinary tar works the products obtained are : Benzene, toluene, xylene, carbolic acid, cresylic acids (cresols), pyridine, naphthalene, creosote, anthracene, pitch. Solvents for special purposes can also be made with great ease, and road naking pitches of any degree of hardness can be produced.

All types of tar receive a similar treatment, but the yields of the valuable products from tars obtained from producers or from vater gas making would not be large enough to make the treatment profitable. Such tars are waste products and difficult to utilise, especially where the percentage of free carbon present is high.

COAL ANALYSIS.

The total weight of the sample of coal should be about 1/40th to 1/80th of the total bulk weight, but when the sample becomes excessively large, the difficulties encountered in breaking it into smaller lumps and intimately mixing it during the operation of quartering detracts from the value of the large samples. As a rule, therefore, a sample of about half a ton is large enough for most practical purposes.*

In order to obtain a small sample from the total sample, the coal should be coned and quartered. This process consists in piling the coal into a circular heap, into which it should be allowed to fall naturally, so that the sides of the pile are the natural angle of rest of the coal. The heap is then divided into four quarters, of which two opposite quarters are taken and discarded, the remaining two are again treated in the same way. As the weight becomes less, it is necessary to reduce the size of the individual lumps of coal, and the following table shows the relationship between the weight of the coal and the size of the largest piece :—

7,000lbs. should pass through a 2in. mesh sieve.
1,200lbs. ,, ,, ,, 1in. ,,
40lbs. ,, ,, ,, 2 ,,
¼lb. ,, ,, ,, 10 ,,

For actual analytical purposes the sample should pass through a sieve of 1/20th inch mesh sieve, and for certain purposes through a much smaller sieve, generally 1/60th inch.

It is important to recognise that during grinding coal loses water very rapidly, and the samples which are finely ground should, therefore, be tested to see whether they have lost moisture.

After the sample has been obtained in the above manner it should be stored in an air-tight bottle and the portion which is used for the analysis should be sealed during the times when it is not required.

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* See "The Sampling of Coal," by F. S. Sinnatt. Bulletin No. 2.

Determination of Moisture.

The amount of moisture present in a coal cannot be accurately determined except by a very cumbersome process, and it is usual, therefore, to employ an empirical process. The process to be described is that advocated by the American Coal Committee, and is the commonest one in use. From 3 gms. to 5 gms. of coal are placed on a weighed watch glass and spread evenly over the surface. The watch glass is then placed in a steam oven, or a hot-air oven, at a temperature of 100° to 104° C. It is allowed to remain for one hour after which it is removed and placed in an atmosphere free from moisture (a desiccator) until it is quite cold. The loss in weight that has occurred is then determined by a second weighing, and this loss is assumed to be the moisture present in the coal. The loss actually consists of moisture ; oxidation, loss of gases ; and gain in weight due to the absorption of moisture during weighing. According to tests made by Archibald and Lawrence the above method may yield results which are 40 per cent. lower than the actual figure. The determination of moisture, therefore, must be considered to be most important owing to the inaccuracies which may occur, and the results are of especial importance if it is required to determine the percentage of hydrogen present in the coal.

The following table affords an idea of what occurs when a sample of coal is heated for an extended period at rather higher temperatures :—

	Gms.
Coal dried at 100° C.	5·0000
After 1 hour at 130°	4·9816
„ 1 „ 175°	5·0346
„ 6 „ 175°	5·2036
„ 3 „ 200°	5·2654

In other words, the coal gains about 5 per cent. in weight due mainly to oxidation. The coal has incidentally lost its caking power. This oxidation may be considered to be the preliminary process which occurs previous to the coal taking fire spontaneously, and it depends upon the rate at which the oxidation will take place as to whether the coal will fire easily or not.

Determination of Volatile Matter and Coke.

This is an empirical test (American Coal Committee)

A platinum crucible weighing 20 to 30 gms. is supported upon a silica triangle above a bunsen burner, the flame of which should be about 8in. long. One gm. of coal, which has not been exposed to the air, is spread evenly over the bottom of the crucible. The lid of the crucible, which should be fairly tight fitting, is replaced, and the coal is heated for exactly seven minutes, with the full bunsen flame. The crucible is then placed in a desiccator to cool and the loss in weight determined by a further weighing. The loss in weight is called *Volatile Matter*, the residue is called the *Coke.*

The Volatile Matter less the percentage of moisture is usually termed *Volatile Organic Matter.* The Coke less the ash is called the *Fixed Carbon.*

The sample of coke left in the crucible at the completion of the test is generally in the form of a small button, and it should be examined and its physical properties placed on record, in fact a sample should be retained for purposes of comparison.

Determination of the Caking-Index or Agglutinating Value.

One gramme of the coal is mixed with gradually increasing unit weights of Calais sand ; the coking test described above is then repeated and the coke examined. When the coal yields a coke which cannot be turned out of the crucible without breaking the weight of sand mixed with the coal is called the Caking Index. Non-caking coals will not hold any sand, whereas good caking coal (*e.g.*, Arley) will hold up to 14 gms. of sand.

Determination of Ash.

One gm. to 5 gms. of coal are spread over a flat silica dish about 2½in. to 3in. in diameter. The coal is then heated gently for a short time and finally heated in a full bunsen or in a muffle until the residue is quite free from organic matter (*i e.*, carbon). The residue left in the dish is the ash in the coal, but it is not the actual inorganic matter present in the coal substance, as during the heating the inorganic compounds present in the coal have decomposed. Nevertheless it is assumed to be the ash in the coal.

Fusibility of the Ash.

A considerable weight of the ash of the coal is required, and it is ground until it will pass through a sieve of at least 1/100in. mesh. A portion of this is taken and made into a paste with water, it is then built into a cone with a square base, having one side vertical. The proportion of the height to the base should be 3 to 1. The cone is then dried in an oven and finally placed in a muffle or other source of high temperature along with a pyrometer. The temperature is gradually raised until the tip of the cone begins to bend over. When this reaches the plane in which the base is situated the ash is assumed to have melted. The temperature is then taken.

The temperature at which the ash will melt or fuse depends upon its composition, but the percentage of iron present has been proved not to have such an influence as was formerly thought to be the case. Thus ash containing the following percentages of iron fused at approximately the same temperature :—

4 per cent. iron oxide (F_2O_3) fused at 2,700°
22 „ „ „ „ 2,300°
40 „ „ „ „ 2,400°

Different portions of the same seam may contain ashes having entirely different fusing points.

Determination of Organic Matter in Clinker.

Owing to the fact that clinker is very hygroscopic, it is not possible to determine the percentage of carbon present in it by simple ignition. It is necessary, therefore, to carry out a combustion upon the clinker, and by weighing the amount of carbon dioxide evolved, determine the carbon present in it. Owing to the fact that all clinker contains a high percentage of sulphur, a portion of which is oxidised, it is practically always strongly acid. It should, therefore, be kept away from all iron materials.

Calculation of the Calorific Value.

A number of formulæ have been suggested for the calculation of the calorific value of coal from the values obtained in the coking test, and one of the best of these formulæ is that devised by Goutal.

Goutal's Formula.

Calorific value in calories $= 82\ C + aV$.

Where "C" is the percentage of fixed carbon, "V" is the percentage of volatile organic matter, and "a" is a constant which depends upon the percentage of volatile matter calculated upon a basis which ignores the ash and moisture.

The following table shows the value of "a" for different values of $\frac{100 \times V}{C + V}$.

$\frac{100 \times V}{C + V}$	"a"
5	145
10	130
15	117
20	109
25	104
30	98
35	94
40	80

Ultimate Analysis of Coal.

The additional values required are the percentage of nitrogen, sulphur, carbon, and hydrogen. When the sum of these is added to the percentage of water and ash, and the total deducted from 100, the difference is the percentage of oxygen present in the coal.

The percentage of oxygen in a coal is of very great interest, as it is generally assumed that when coal is carbonised or burnt, the oxygen present in it combines with hydrogen at once. From this it is obvious that the hydrogen available for gas-making is the total percentage of hydrogen less the amount which is combined with the oxygen. This is called Disposable Hydrogen.

The following example explains this point :—

Analysis of a fairly good coal.

	Per cent.
Water	4·3
Ash	6·7
Sulphur	1·3
Nitrogen	1·4
Carbon	72·9
Hydrogen	4·7
Oxygen (By difference.)	8·7

The hydrogen which will combine with 8·7 per cent. of oxygen can be calculated from the fact that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen to form 18 parts by weight of water.

$$\begin{gathered} H_2O = H_2O \\ 2 + 16 = 18 \end{gathered}$$

Therefore, to combine with 8·7 per cent. of oxygen, 1·0 per cent. of hydrogen is necessary; as the coal contains 4·7 per cent. of hydrogen, the disposable hydrogen is 4·7—1, *i.e.* 3·7 per cent. It is frequently found that coal otherwise suitable may contain a low percentage of available hydrogen.

Determination of the Calorific Value.

There are a number of methods for the determination of the calorific value of coal, of which two will be mentioned. The first is an empirical process and depends upon the combustion of coal by means of sodium peroxide. It is called the Roland Wild method. A description of this method can be obtained from Messrs. Alexander Wright & Co., Westminster, London, S.W. The main point to be remembered is that the coal should be powdered to a degree of fineness which depends upon the particular nature of the sample. Soft coals should be used in rather a coarse powder, whilst hard coals should be ground to pass through a sieve of 1/60m. mesh.

The method has a second feature, namely that after the coal has been burned in the nickel crucible by means of sodium peroxide, the residual mass contains the whole of the sulphur present in the coal as sodium sulphate. It forms, therefore, an extremely rapid method for the determination of sulphur in coal. The mass is dissolved in water, made slightly acid with hydrochloric acid, and the solution of barium chloride is then added. A white precipitate of barium sulphate is formed, this is filtered off through a filter paper and washed with hot water. The filter paper and precipitate are then dried completely, and finally the filter paper and precipitate are placed in a weighed crucible. The whole is then ignited, when the filter paper burns and leaves behind the pure barium sulphate. From the weight of the barium sulphate the percentage of sulphur can be calculated, assuming that 233 parts of barium sulphate contain 32 parts of sulphur.

For a description of the Bomb Calorimeter, see Catalogue of Cook, Instrument Maker, The University, Manchester.

Occluded Gases.

The gases contained in the pores of the coal substance, the so-called occluded gases, are of very considerable importance from many points of view. The gases can be driven off by heating the coal in water or by placing it in a vacuum. Anthracite contains methane and ethane; steam coal contains methane, carbon dioxide, oxygen, and nitrogen Bituminious coal contains methane, carbon dioxide, oxygen, and nitrogen. Lignite contains chiefly carbon dioxide and a little methane. Peat contains carbon dioxide and occasionally carbon monoxide.

The subject of the absorption of air and oxygen by coal is not thoroughly understood, and the following example shows the composition of the gases drawn off from coal (a) when obtained fresh from the face, and (b) when the same coal had been exposed to the air for a few days.

	Fresh (a) Per cent.	After exposure to Air (b) Per cent.
Carbon dioxide	1·6	1·2
Oxygen	8·8	23·8
Methane	44·6	3·6
Nitrogen	44·7	71·4

The curious point in the above tables is that the percentage of oxygen (23·8 per cent.) is higher than that present in ordinary air (20·9 per cent.), and it would, therefore, seem that the coal absorbs oxygen much more quickly than it absorbs nitrogen.

The Storage of Coal.

This subject is allied with that of the spontaneous combustion of coal. The following is a summary of the main points in connection with the spontaneous combustion or oxidation of coal, drawn chiefly from the work of Parr and Walker.

(a) Oxidation begins at ordinary temperature.
(b) Below a certain temperature coal will not fire.
(c) As soon as the coal reaches this temperature the oxidation cannot be stopped (auto oxidation).
(d) When the temperature goes up still higher, it reaches the ignition point of the coal; generally at about 350° C.
(e) Heat from external sources should be prevented from reaching the coal (*e.g.*, the sun's rays, hot pipes under the floors, heat of impact in piling, friction of the particles).
(f) The fineness of coal has an especial influence upon its oxidation and a mixture of fine coal and lump coal is especially dangerous.
g) Iron pyrites are not of importance until the temperature of the coal has reached a certain critical figure, but as soon as the oxidation of the pyrites begins, the combustion of the coal will proceed rapidly.
(h) The presence of moisture promotes the oxidation of coal.
(i) The oxidation of carbon and hydrogen begins at a very low temperature—namely, at 120° C.

A consideration of the above points has led to the general conclusion that coal should not be piled to a greater height than 12ft., and that some coal will oxidise spontaneously when heaped to a height of 6ft.

The ideal system of storing coal, and one which obviates all difficulties, is to store it under water. This has been practised to some extent in America and Germany, and has been found to be extremely economical. The main objection is the time required for the coal to dry.

The Buying and Selling of Coal.

Standard specification of the London Municipal Electrical Engineers and the principal London Coal Contractors, a committee representing the above bodies decided upon a standard specification for the purchase of coal This was published in the "Coal and Iron Trades Review" for March 28th, 1913. It describes the method of analysis, the conditions of purchase as to time, the reduction in price due to the variations in the analysis, &c.

The City of Chicago purchases its coal upon a specification which requires them to receive 100,000 B.T.U. for each cent; in other words, coal at 13s. 4d. per ton, assuming it to be 14,000 B.T.U.

Carbonisation of Coal.

The manufacture of coal gas; the process of coal gas manufacture is one in which coal is subjected to distillation at a high temperature in either horizontal or vertical retorts. Although vertical retorts are rapidly replacing horizontal retorts, the latter must not be considered obsolete, as they have a certain distinct function of their own. The retorts are heated to at least 800° C, and, as a rule, to 900° C. and 1,100° C. The source of heat for the retort is by burning producer gas on the outside of them, the producer gas being made from part of the coke obtained in the process. The product aimed at on gas works is coal gas, and the main part of the process consists in the purification of the impure coal gas In the case of coke manufacture the product worked for is coke, and the coal gas is a by-product and generally used for heating the retorts. The products obtained when coal is carbonised are the same in all cases, but the composition of the products is different, depending upon the process used. Essentially the products are coke or residue, coal tar, water, and gas.

High temperature carbonisation of coal (900° C. to 1,100° C.) as in gas and coke making.

	Yield per ton of Coal.
Gas..	9,000 to 13,000 cub. ft.
Tar	11 to 14 gallons.
Ammonia (expressed as Ammonium Sulphate)	Up to 30lbs.
Coke	Ordinary gas or foundry coke. Hard, difficult to ignite.

Description of Gas Manufacture.

The coal is crushed and charged into retorts generally (in pre-war times) 7 cwts., and heated for 6 hours. Nowadays, the amount is 10 cwt. to 12 cwt. heated for 10 hours to 12 hours.

The whole of the products of carbonisation, tar, water, and gas, pass up the ascension pipe to the hydraulic main, which is usually sealed with water. Here much of the tar is deposited. The gas then passes through air or water condensers where it is cooled, and a further portion of the tar is deposited. The gas enters an exhauster or compressor, where its pressure is raised sufficiently to enable it to pass through the remainder of the purifying process. It is then forced through a washer-scrubber in which it is washed by contact with water and yields ammonia liquor. This liquor is then sold to a distiller or treated on the gas works, and ammonium sulphate recovered from it. This is the most important by-product of the gas works.

The gas still contains sulphuretted hydrogen, which is removed by treating it with hydrated oxide of iron, the latter generally being mixed with sawdust or wood shavings to increase its porosity. Where there is a market for spent lime, hydrate of lime or slaked lime is sometimes substituted for hydrated oxide of iron. Spent lime is used as a fertiliser, but in large towns difficulty is experienced in finding a sale for it, and therefore oxide of iron is used The gas is then treated in a washer with heavy oil or creosote in order to recover the benzene and toluene (during war time). If the gas contains naphthalene, it is necessary to wash it to remove this impurity, otherwise it is deposited in the pipes, and will prevent the free passage of the gas.

Coal gas is not generally sold in the pure state, but is mixed with carburetted *Water Gas*, usually about 20 per cent. of the latter gas is added. The mixture of water gas and coal gas is called Town's Gas.

Composition of Blue Water Gas.

	Per cent.
Carbon dioxide	6·0
Carbon monoxide	43·0
Hydrogen	48·0
Methane	0·5
Nitrogen	2·5

Coal gas	Ordinary Retorts.	Vertical Retorts.
Carbon dioxide	2·0	2·0
Oxygen	0 3	Nil.
Carbon monoxide	6·0	9·0
Unsaturated hydrocarbons	4 0	3·0
Methane	33·0	32·0
Hydrogen	48·0	51·0
Nitrogen	6·7	3·0

Water Gas.

Water gas is made by passing steam through red-hot coke; this yields blue water gas, which afterwards is usually enriched with cracked oils or carburetted.

Coke contained in a large generator is blown into a state of incandescence by means of an air blast of 20in. to 30in. of water pressure; time of blast 1 minute to 4 minutes. When the required temperature has been attained steam is forced into the incandescent coke; the time being for the English process 6 minutes, for the Delwik process 8 minutes. The result is that the coke decomposes the steam and yields water gas, which, theoretically, is a mixture of 50 per cent. carbon monoxide and 50 per cent. hydrogen, and has a calorific value of about 330 B.T.U. per cubic foot. Usually this gas, which burns with a colourless flame, and is called Blue Water Gas in consequence, is carburetted. Two processes of carburetting are in common use. The first is to add benzene or petrol vapour; the second is to crack petroleum (solar oil fraction) and mix the resulting oil gas with the water gas. Afterwards, the water gas has to be purified in much the same manner as coal gas, but the process used is not so complicated.

Producer Gas.

Two types of Producer Gas are common—Suction Producer Gas and Power Gas

Suction Producer Gas is made from many kinds of fuel, the essential property of which should be that they do not yield a large proportion of tar when carbonised The best fuels are anthracite, coke, wood, peat, &c The fuel is introduced into the producer and the gas is made by the suction action of the gas engine itself. Theoretically, the gas should contain 34 per cent. carbon monoxide and 66 per cent. nitrogen, but generally water or steam is introduced which alters the composition of the gas and yields one which is a mixture of producer gas and water gas, *e.g.*, carbon monoxide 25 per cent., hydrogen 6 per cent., carbon dioxide 5 per cent., methane 1 per cent., nitrogen 63 per cent., shows a semi-water producer gas.

Theoretically the calorific value of producer gas is about 110 B.T.U to 113 B.T.U. per cubic foot, but by using the correct volume of water the calorific value may be 140 B.T.U.

Suction producer plants are made from 2½ h.p. up to 250 h.p. but above this size they have not, up to the present. been a success.

Power Producer Gas.

These producers may be of any size, and the best example is the Mond producer. The essentials for the success of the process are to have an ample supply of air and steam under pressure.

Mond Producer Gas

These producers are generally made to deal with about 20 tons of coal in 24 hours, and in order to increase the size of the installation additional producers are installed The essentials for the success of the process are, careful control of the temperature in the producer with a view to the prevention of the decomposition of ammonia. The ammonia that is formed has then to be recovered from the producer gas. It is recovered as ammonium sulphate directly from gas, by treating it with dilute sulphuric acid. When the specific gravity of the sulphuric acid has reached a standard figure indicating the presence of ammonium sulphate in solution, it is removed from the washer or dasher in which it is contained, and evaporated until the ammonium sulphate crystallises out. Such ammonium sulphate is practically the same commercial value as that obtained from the gas works.

Low Temperature Carbonisation.

None of the processes devised up to the present can be considered to be completely successful; the chief processes described in the literature are the Delmonte process, the Tarless Fuel

Syndicate Process, the Coalite Process, the Maclaurin Process. In all these methods coal is carbonised at a temperature not exceeding about 550° C. The object all such processes have in view is to produce a smokeless fuel or coke which will be a scientific substitute for coal, *i.e*, burn with a smokeless flame and ignite readily. Secondly, to obtain a greatly increased yield of tar, which would possess special properties. The constitution of such tars is entirely different from ordinary coal tar. On distillation instead of the aromatic series of hydrocarbons those of the methane, ethylene or acetylene series would be obtained. This would form a valuable motor fuel. The yield of ammonia from such processes promises to be greater than is produced during high temperature carbonisation. View broadly, the process of low temperature carbonisation appears to be one which could be combined with that of ordinary coal gas manufacture with great advantage to both industries. The results would probably be beneficial to all users of fuel in open grates, would decrease the smoke nuisance, and economise the nation's coal. (See Smoke and Town Air, Cohen and Ruston; Arnold, London.)

Low Temperature Carbonisation. (450° C. to 600° C.)

	Yield per ton of coal.
Gas . . .	2,000 to 4,000 cub. ft. (high calorific value).
Tar . . .	15 to 40 gallons
Ammonia .	Up to 8lbs. per ton.
Smokeless Fuel .	Specimens examined up to 12 per cent. volatile matter.

Del Monte Process.

The apparatus consists of the following train of plant: Retort, producer, condenser, scrubber, gas holder, compressor, and re-heating coil. The main idea of this process—and on it is based the process of Maclaurin—consists in carbonising the coal by heating it with inert gas. The coal is placed in the retort, which is heated by means of a producer. The gas which is evolved from the retort passes through the condensers and scrubbers and into the gas holder, from which it is sucked by means of a gas compressor and then forced through a heating coil which is situated round the retort. It is there raised to a high temperature and then passes into the bottom of the retort and aids the carbonisation of the coal and facilitates the removal of the low temperature carbonisation products. The temperature of the retorts is usually 450° C. to 550° C.

The Maclaurin Process.

This process is very similar to the Del Monte Process, but, instead of the coal gas being circulated round and round the plant, producer gas which has been heated is used to carbonise the coal. The temperature is 450° C to 550° C.

The Tarless Fuel Syndicate Process.

The coal is carbonised in cast-iron vertical retorts under a diminished pressure or vacuum of 12in. to 25in of mercury at a temperature of 450° C. to 550° C. The patent lies in the design of the retort and the use of a high vacuum.

The Coalite Process.

This process is very similar to that used in the ordinary gas works, except that the carbonisation is carried out at a temperature of about 450° C., and steam is introduced into the retort during the process. The result is a semi-carbonised coke which will burn with a smokeless flame.

Books to Consult.

In the course of the lectures a brief summary was given of the contents of the following books —

Treatise on Petroleum B Redwood (Griffin & Co , London)
Petrol and Petroleum Spirits. Guttentag (Arnold, London.)
Coal, Its Composition and Analysis Somermeier (McGraw, Hill & Co)
Carbonisation of Coal Lewes. (Benn Bros , London)
Constitution of Coal Stopes & Wheeler (H M S Stationery Office.)
Coal and Its Scientific Uses Bone (Longmans Green)
Modern Coking Practice Christopher & Byrom. (Crosby, Lockwood & Son)
Chemistry of Gas Manufacture. Royle (Crosby, Lockwood & Son.)
Coal Gas Residuals. Wagner (McGraw, Hill & Co.)
Coal Tar and Ammonia. Lunge. (Gurney, Jackson)
Handbook on Briquetting Franke and Lantsberry. (Griffin & Co., London.)

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

The SAMPLING OF COAL

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PRICE
ONE SHILLING

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PREFACE

Although much has been written upon the subject of Coal Sampling, the information is not readily accessible to those who are interested in the sale and purchase of coal.

The standard works on coal do not deal with the subject adequately and leave far too many points indefinite which should be standardised.

The sampling of coal is the most vital feature in arriving at its true value, and unless merchants, consumers, and the collieries agree to a standard method, it is useless to attempt to buy and sell coal on the basis of its calorific value and chemical analysis.

It is hoped that the matter contained in this bulletin may assist in the evolution of a standard method of sampling coal to replace the present haphazard methods.

Suggestions and criticisms are cordially invited and will be acknowledged in any further editions.

R. A. BURROWS,
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THE
SAMPLING OF COAL

Introduction.

In certain industries the purchase and sale of coal is in the hands of the commercial and engineering departments only, and little attempt is made to determine the actual value of the coal by analysis.

The majority of progressive firms, however, now require the coal they are purchasing to conform to certain standards.

That there are great natural variations in the quality of coal, even from the best collieries, is common knowledge. A seam may vary in the same mine, and the practice of having the coal examined at frequent intervals as it is received at the works, is becoming very general. Many firms, also, are now having their coals analysed regularly by outside analysts, and in view of these facts, it is of importance that everyone connected with the purchase or sale of coal should be thoroughly alive to the importance of the subject of sampling and to its difficulties and that a common method should be adopted.

The subject is intimately related to the work of the chemist who has to carry out the chemical analysis of the coal or the determination of its calorific value, and it is natural to suggest that wherever possible the chemist should have charge of the operation of sampling, or that he should be present while it is being carried out. As much care should be expended on the operation of sampling as upon the actual analysis of the coal, and the cost of obtaining the sample should not be less than that of the analysis.

It is obvious that unless the sample taken from the whole consignment of the coal is representative of the entire weight, the values found by the analyst will not represent those of the whole consignment The results of inaccurate sampling are extremely far reaching and, in addition to the financial loss which may be entailed, much trouble may be caused by the fact that the results of practical tests on the coal will not agree with the figures obtained by the analyst. The results of boiler trials and inaccurate heat balance sheets are frequently extremely difficult to explain, and one of the chief sources of the disagreement lies in the fact that the coal used in the trials is different in calorific value from the actual sample sent for valuation by the analyst

The only method by which such errors can be eliminated is to place the whole operation of collecting the sample under the most stringent supervision.

Principle underlying Sampling and the possible errors.

To be truly representative of the whole weight of any consignment of coal, a sample should not only contain a portion from every different part of the coal, but also the correct proportion of large and small coal, and of large and small pieces of foreign matter or impurities.

The errors introduced by the above requirements being overlooked are far greater than those possible even by slipshod chemical analysis, and the following example quoted by Bailey (Jour Ind Eng Chem. 1909, p 161-178) shows the variations in the percentage of ash present in coal which are possible by improper sampling (The methods of sampling adopted in this case were seemingly correct.)

Three tons of coal (run-of-mine) were collected in a heap and then shovelled into barrows; from each barrow, when full, 16 separate shovelsful were taken and placed in 16 separate sampling barrels. This process was repeated until each of the barrels contained about 125lbs. The 16 samples were treated in exactly the same manner; each was broken into small pieces, mixed thoroughly, and then quartered repeatedly until a small sample, suitable for analysis, was obtained.

The percentage of ash present in each of the 16 samples was then determined, with the result that a difference of 3·24 per cent. was found between the highest and lowest determinations, the average ash content being 10·68 per cent.

It is clear that although each of the above samples appears to have been obtained in a similar manner, the percentages of ash present in certain parts of the coal must have differed widely

The explanation of the variation lies in the fact that a proper proportion of large and small coal and lump and small foreign matter was not obtained in removing the shovelsful from the different barrowsful

The following examples, which have come to the Author's notice during the past four years, are chosen as representing typical examples of inaccurate sampling :—

(1) A sample, weighing about 1½lbs., was stated to be a representative sample of a consignment of some hundreds of tons. The sample was in the form of a fine powder, but contained two large pieces of stone, each weighing 1 oz. The sample was analysed with and without the pieces of stone present, with the following results

	Per cent
Ash with the stone present . ..	20·6
Ash with the stone removed	12·2

The two pieces of stone were added as the sample was taken, on the assumption that they represented a proper proportion of the stone present in the coal. If the consignment had contained the amount of stone represented by the two pieces, each ton would have had about 1½ cwt. of white stone in the form of lumps, actually it contained very little

(2) An Engineer responsible for a boiler installation was invited to submit a sample of the coal he was using for analysis. Permission was then obtained to take a representative sample of the same coal. The following results were obtained :

	Per cent.
Ash present in Engineer's sample ..	5·0
Ash present in a representative sample..	15·0

(3) A sample received for analysis weighed about 4 oz and was said to be a sample of coal received from five collieries. It was stated to have been obtained by taking a handful from a heap of each of the different consignments of coal, and mixing the specimens together.

The samples mentioned above are quite valueless, and suffer especially from the fact that the weight of the sample is too small to have represented the total weight of coal.

Weight of the Sample.

The greater the weight of the sample, the more representative it will be of the bulk weight of the coal, thus the errors due to the weight of the sample are shown in the following table

Weight of sample Pounds	Actual error in the percentage of ash.
125	3·24
250	1·61
600	0·93

The wider the variation in the size of the pieces of coal, the larger must be the sample , this also applies to the foreign matter present Bailey has shown (*loc. cit*) that the weight of the sample should bear a direct relationship to the size of the largest piece of foreign matter present, and to insure an error of less than 1 per cent. in the ash present in the sample, the following must be adhered to

Size of largest piece of slate (or shale) in inches.	Original sample must weigh Pounds.
4	39,000
3	12,500
2	2,800
1½	1,900
1¼	1,200
1	600
¾	230
½	90

As a rule it is considered that the gross sample should be from 1/40th to 1/80th of the total weight of coal This rule is quite satisfactory so long as the gross sample does not exceed about 1,000lbs. When it does exceed that amount, the inaccuracies introduced during crushing, mixing, and the quartering of the sample become excessive.

The weight of coal carried by an ordinary coal shovel varies from 12lbs to 25lbs., and this is generally accepted as the smallest unit to remove during sampling, when dealing with lump coal. In the case of slack or small washed coal up to nut size this weight is too great, and a smaller shovelful of about 5lbs. should be adopted as the unit for the sample. When dealing with large lumps a number should be broken and the unit taken from the broken portion. This should be repeated wherever the lump, which should be removed as part of the sample, has a greater weight than the unit weight of the sample.

Difficulty will be experienced in determining the most suitable weight for the gross sample, but it should be assumed that the smallest weight is 1,000lbs. for bulks weighing about 100 tons, *i e.*, about 1 part in 200. The weight of the sample should not be reduced much below 250lbs. for a truck of coal; for, assuming that a shovelful of coal weighs 15lbs., this means that only 16 units are collected from 10 tons of coal. Either the sampling shovel should be reduced in size or a larger gross sample should be collected If dealing with lumps the former is not sound, hence a larger sample is desirable If a number of trucks of coal from the same source have to be sampled, the weight of the sample, say 1,000lbs., is determined upon and the necessary fraction is taken from each truck. A separate gross sample should be collected for each distinct change in the type or source of the coal Further, it is more accurate to take a number of gross samples and deal with them separately, than one sample, and have the sampling proportion very high. A sample of about 1,000lbs in weight is large enough for most practical purposes, but larger weights can be handled with ease if a mechanical sampler or a small coal crusher is available (see page 14).

In obtaining the gross sample great care must be exercised to ensure the presence in it of the proper proportion of large and small coal and of large and small impurities. This may be checked approximately by carrying out a test before the sample has been crushed to determine what proportion of the sample will pass through, say, a sieve of ¼in. mesh This test indicates the proportion of small coal present in the consignment; it also forms one of the simplest checks on any further deliveries. If the percentage of fine coal differs widely from that present in the original sample, then variation in the quality may be expected.

In the Standard Coal Specification (see page 12) there is a clause specifying the limiting percentage of small coal permitted in deliveries of coal. The methods of testing are indicated in the following table, showing the requirements for Bituminous Coals, washed and dry screened from Durham and Yorkshire

Dry Screened Coals	Moisture Per cent	Size of Square Mesh	Percentage of Small Coal passing through
1. Double Nuts 12,750 B.T.U	5	½in.	17½
2. Single Nuts 12,500 B.T U	6	⅜in.	25
3. Peas 12,250 B.T.U.	6	¼in	25

Washed Coals.	Moisture. Per cent.	Size of Square Mesh.	Percentage of Small Coal passing through.
1. Washed Double Nuts 13,250 B.T.U.	8	¼in.	15
2. Washed Single Nuts 13,000 B.T.U.	9	⅜in.	17½
3. Washed Peas 12,750 B.T.U.	10	¼in.	20

Taking the Sample.

It is practically impossible to obtain a representative sample from the surface of a heap of coal, and this applies to all stationary masses of coal (trucks, barges, carts, &c.). The only satisfactory method is to collect the sample as the coal is being distributed in small units or collected in a large mass, by successive small increments, this applies to every case. Thus, the sample should be obtained by taking a shovelful from each barrow or small truck as the coal is being removed from, say, a railway truck or barge, or a shovelful should be taken during unloading and collected in a special box or barrel. It should be recognised that when coal has been transported or undergone any vibration when in the mass that a large proportion of the fine material will have found its way to the bottom of the mass

In order not to interfere unduly with the work of the men unloading, it is preferable to let a special man take a shovelful as the barge, truck, or cart is gradually unloaded or loaded, the shovelful being taken as regular fractions of the bulk are removed or added It is by this means only that portions from every part of the mass of coal can be obtained, and that a proper fraction of the large and small coal can be ensured

When samples are required to represent a seam of coal, by far the most satisfactory solution is to cut a pillar of coal through the whole depth of the seam, about 6in wide, and 6in to 8in. deep, and including a portion of roof and floor This is then placed in a box constructed for the purpose, slightly larger than the pillar of coal, and the whole kept in position by wooden wedges and clean straw Each break in the coal should be marked with a white number from the roof to the floor Such samples have been obtained from seams 9ft thick, and the exhaustive examination of the coal could be carried out with complete confidence Sections should be obtained wherever any visible change in the seam occurs or at stated intervals The results obtained by the analysis of such samples, combined with routine analysis of the output, enables the colliery to keep a complete check on the process of purification of the coal and on the complaints of consumers.

Treatment of Gross Sample.

During the period of collection the sample should be stored in a situation which is free from dust (especially coal dust), rain, draughts, and not liable to rapid changes of temperature. A covered barrel or box is suitable for the purpose, or a small room or covered shed.

After the sample has been obtained it must be mixed frequently and efficiently, and crushed at intervals. It is a great convenience, therefore, to place the sample upon a sheet-iron sampling plate on which it is possible to crush the coal. A "punner" or large hammer will be found to be one of the most handy forms of coal crusher for this coarse grinding The process of crushing, &c, should not be carried out on a brick or stone floor if there is any chance of foreign matter being introduced from this source. A second method is to place the whole of the sample on a thick canvas, cloth sheet (coarse satin), or tarpaulin, on which it may be crushed by means of the punner or hammer; the coal may also be mixed by bringing the corners of the sheet across and back again and repeating the operation a number of times.

Coning and Quartering.

To ensure perfectly unbiased mixing of the gross sample and at the same time to reduce its weight until it is convenient for the laboratory, the following process of coning and quartering must be rigidly observed

The sample is thoroughly mixed and thrown into a heap having a circular base by means of a shovel, the coal being allowed to fall to the natural angle of rest. The heap will form a rough cone.

The cone is now completely flattened, and the flat heap divided into four separate quarters by cutting two distinct trenches through it at right angles to one another. Two opposite quarters are removed and rejected, the dust from them being cleared away by means of a brush. The remaining two quarters are collected together and intimately mixed by the aid of the cloth. The coal is again thrown into a cone and the process of quartering repeated until the residue is the desired weight.

In carrying out the above operation it is necessary to crush the coal as the weight of it decreases.

The following table shows the size to which the sample should be broken in order to eliminate errors during the reduction of the weight of the sample.

Weight of Sample to be Quartered. Pounds		Greatest Size of Pieces of Coal and Foreign Matter. Inches.
3,800	..	1½
1,200	..	1
460	..	¾
180	..	½
40	.	2 mesh.
5	..	4 „
½	..	8 „
¼	..	10 „

Laboratory Sample.

The above principle cannot be ignored in the laboratory, and the following are the limits beyond which the samples should not be quartered for various sizes of the pieces of coal —

Size of Coal Mesh.		The sample should not be reduced to less than Grams.
2	..	8,300
4	..	1,100
8	..	120
10	..	55
20	..	3

When the weight falls to about 40lbs. the sample may be sent to the laboratory, or be crushed so as to pass through a sieve of four meshes to the linear inch, and its weight reduced to about 15lbs. It should then be divided into three portions, the first for the laboratory, the second to be sealed and preserved in case of disputes, and the third to be sealed and preserved for examination by a neutral expert in case this becomes necessary For most practical purposes the last sample is omitted, but the two former are essential owing to the variations which may occur during the storage of the coal. A complete history of the sample should be attached to it and be added to the analyst's report.

The following is the clause on sampling from the Standard Specification on coal which was prepared by a committee representing the principal London firms of Coal Contractors and the Associated Municipal Electrical Engineers of Greater London (Coal and Iron Trades' Review, 28th March, 1913) :—

"A representative sample shall be taken on delivery from each and any consignment and shall be divided and sealed in three air-tight vessels. The contractor shall be at liberty to be represented when the sample is taken and shall be entitled to one portion thereof. The contractor shall have no opportunity at a later date of objecting to the manner in which the coal has been sampled."

Samples may be preserved in porcelain or glass, jars fitted with patent air-tight lids (*e g.* preserve bottles) ; samples to be used for analysis should, however, be kept in glass-stoppered bottles.

It is important to recognise that precautions must be taken in the preservation of coal samples in order to prevent any variation in the moisture present.

It may be pointed out that recent experiments have shown that the percentage of moisture in coal varies with the degree of humidity of the air, and that the change takes place very rapidly, depending upon the weight of the sample and its state of division. In certain cases it has been found that the percentage of moisture in coal may vary by at least 0·5 per cent. during a period of six hours.

The following figures, from among others, are quoted to emphasise this point —

Coal	Mesh	Time	Moisture per cent.	Degree of Humidity.
Arley (Wigan)	30's	9-46 a.m.	2·19	88·0
,,	,,	7-0 p.m.	2·08	73·0
,,	180's	9-46 a.m.	3·03	88·0
,,	,,	7-0 p.m.	2·56	73·0
Indian	30's	10-40 a.m.	4·30	73·5
,,	,,	3-50 p.m.	4·75	79·5
,,	200's	10-40 a.m.	4·36	73·5
,,	,,	3-50 p.m.	4·76	79·5
Peat	30's	9-20 a.m.	14·40	68·8
,,	,,	3-45 p.m.	13·75	63·6
,,	200's	9-20 a.m.	13·60	68·8
,,	,,	3-45 p.m.	13·04	63·6

(*Sinnatt and B. Moore, unpublished paper.*)

The sample for use in the laboratory must be crushed so as to pass through a sieve of 20's mesh, and it is important to notice that in all the crushing and grinding the whole of the sample should pass through the sieve It is well known that with certain types of coal the foreign matter can be powdered more readily than the coal, whilst with other coals the reverse is true It follows that a portion of the coal should not be rejected if, during sieving it is found to be difficult to powder. It is the practice in certain laboratories to sieve the sample during grinding, and when the weight required has passed through the sieve, to take this for the analysis, and reject the residue. This yields results which do not represent the actual bulk of the coal in any respect.

The grinding of a small quantity can be carried out in a grinder of the type of a coffee mill, but care should be taken to obtain one which can be easily dismantled for cleaning purposes or be of simple design An air blast will be found an efficient method of cleaning such apparatus.

For certain of the chemical determinations (*i.e* for the estimation of nitrogen and sulphur) it is convenient to have the coal in a very fine state of division, and a grinder which has been found to be very useful is a small ball mill. Such a mill consists of a porcelain cylinder about 6in. diameter and 8in.

long, partly filled with irregularly-shaped porcelain balls. The cylinder may be made to revolve at any desired speed. If required, coal can be powdered so as to pass through a sieve of as fine as 200's mesh in a few hours. It is possible to grind coal in such a mill without continually exposing it to the air, and, in consequence, little change due to oxidation takes place in the coal during the process.

Mechanical Sampling.

The methods of sampling described above are those which can be carried out by hand. The efficiency of the operation is increased by the use of the following plant :—

A mechanical coal crusher, by means of which the coal can be broken to any degree of fineness.

A riffle, by which the operation of coning and quartering can be eliminated.

A machine of the type of the Sturtevant Coal Crusher and Sampler. The operation of sampling is greatly simplified, and larger samples can be easily treated. This machine consists of a coal crusher to which is attached an arrangement for taking any desired fraction of the coal passing through the crusher. The degree of fineness of the coal may be varied by a simple adjustment. The machine will deal with up to one ton per hour. In sampling with the machine it should be recognised that the coal must be intimately mixed before it is fed into it. The fraction of the gross sample separated should also be thoroughly mixed.

When large weights are being dealt with, it is advantageous to pass the sample through the plant a number of times and thus gradually decrease its weight, the coal should be mixed between each of these treatments

The chief part of the Board of Trade leaflet on Coal Sampling is attached for reference, as it is not possible to make an abstract of an adequate nature —

COAL SAMPLING FOR ANALYSIS.

Hints on the best method of obtaining thoroughly representative Samples.

1 *General.*

The importance of ascertaining the Calorific Value of fuel used in any particular works cannot be over-estimated It is quite impossible to control intelligently the thermal efficiency of any plant unless means are taken to establish the Calorific Value of the coals used. Far too little attention has hitherto been paid to the question of sampling, whereas, *however carefully the analysis is taken, the final result will be of little value unless a thoroughly representative sample has first been obtained* When one considers that the heat value of a particular consignment of fuel is ultimately determined on about one ten-thousandth part of a 20lb. sample, it will be appreciated how easily an error of 1,000 to 2,000 B.Th U 's can be made if the sampling is not carefully attended to.

As indicating the importance of the necessity for careful sampling the following instance may be given :—

A slack coal recently received from a Midland colliery gave no indication from appearance of being anything abnormal. On separating the small from the large, however, the small was found to contain 10 per cent. of ash, whereas the large contained 40 per cent of ash. *What would be the worth of an analysis as representing the heap from which a sample had been taken if the proportion of large and small received in the laboratory had not been representative of the large and small in the heap?* Let us assume that in the heap from which the sample was taken the percentage of small was 25 per cent. This would give a total ash content of 32·5 per cent., namely, 25 per cent. with 10 per cent. of ash and 75 per cent with 40 per cent. of ash. Now, if the sample sent to the laboratory contains 75 per cent. of small, the total ash content of the sample would be only 17·5 per cent., namely, 75 per cent. at 10 per cent and 25 per cent. at

40 per cent It will be seen at once that the Calorific Value as disclosed by the laboratory would vary tremendously in the two samples referred to

2. *How to take Preliminary Samples.*

To obtain as nearly a representative sample of the bulk as possible the following procedure should be adopted .—

(a) *Large Screened Coal*

The sampling of large screened coal is perhaps the most difficult with which the fuel analyst has to contend. The consignment may contain anything from 5in. or 6in. cube up to 12in., 15in., or even larger pieces. The best plan is by carefully inspecting a consignment of, say, 10 tons, to pick out fairly representative pieces to the extent of about 10 per cent. These pieces should then be broken, and again, by a further selection, about 10 per cent. separated from the bulk. This smaller sample should be further broken and thoroughly mixed, after which a final sample of about 10lbs can be selected for the laboratory.

(b) *Large Unscreened Coal (Through and Through).*

Separate about half a ton into two heaps, one containing the large and the other the small, in order to ascertain their respective percentage by weight. If, for instance, the coal contains 50 per cent of large and 50 per cent. of slack, a proportion of the larger pieces should be dealt with as described under the heading of "Large Screened Coal," and the slack dealt with in a similar manner to that described below.

(c) *Graded Coal (Nuts, Beans, Peas, &c.).*

This is the simplest class of fuel from which to obtain representative samples, as a few shovelfuls from various parts of the main heap are all that is usually necessary.

(d) *Slack Coal.*

To obtain a really reliable sample of slack coal from a given heap it is advisable to start with a fairly large quantity. Where trucks or carts are being continually received and unloaded three or four or more shovelfuls of the fuel should be taken from different parts of each load and thrown on to a common heap. When the testing sample has to be taken this heap should be carefully trimmed round at the edges, the coal so trimmed being thrown into the centre so as to form a rough cone. This cone should then be flattened by means of a straight board twisted across the top of the heap until it becomes a flat disc of, say, 2ft. thick. This should then be divided into four, or what is known as "quartering," and the two opposite segments removed. The remainder should then be remixed and treated as before to obtain a final sample of about 20lbs. weight for slacks of 1in. and under, or 40lbs weight for rougher slacks

3. *Weight of Samples for Laboratory Tests.*

The final sample forwarded to the laboratory should never be less than 10lbs. in weight, and in dealing with difficult fuels—amongst which are included nearly all slacks—it is desirable to increase this up to 20lbs or even 40lbs.

4. *How to Deal with Laboratory Samples.*

We will describe the best method to be adopted with a difficult sample of slack fuel at some length. With crushed coal and more consistent grades experience will show that some of the stages may be omitted, but it is best to begin with too much attention to detail rather than too little

Before attempting to reduce the sample as submitted to the laboratory to suitable dimensions for actual test, it is essential that the surface moisture should be taken from it. This can best be done by recording the weight of the whole sample, which should then be left on a large tray spread out in a very thin layer for, say, 48 hours This air drying is necessary for two reasons. Firstly, the total moisture cannot otherwise be correctly ascertained, as the coal will be losing moisture during sampling; and, secondly, it is otherwise impossible to get a good mixture, as the small damp coal and soft shale will cling together and not mix with the dryer coal when it is ground.

It is wrong to rob the laboratory sample of a part for separate moisture determination, as is frequently done, inasmuch as this would have to be done with little or no crushing of the larger coal, and would not only be unrepresentative of the remaining moisture content, but may also be robbing the remainder of an undue portion of either clean coal or shale

After being exposed, as suggested above, for 48 hours in the room in which the further sampling is to be carried out, the coal will be at equilibrium with the atmosphere, and in this condition can be safely ground and mixed without either losing or gaining moisture.

Grading the Sample.

It is often very difficult to thoroughly mix a sample of ground coal weighing 20lbs. It may be thought that if the whole sample is ground and mixed that no better way can be adopted. This is not so. If such a scheme is adopted it will be found that after several hours' stirring and mixing has taken place, streaks of varying colour indicating varying quality will still remain, and it is quite impossible to take the two ground Calorimeter Samples from any part of the 20lb. heap and be sure that they fairly represent the bulk.

The following will be found a very satisfactory method of overcoming this difficulty :—

Separate the 20lb. sample by means of sieves, carefully noting the weights and proportions of each. The following is an example of the method :—

		Proportion per cent.
(a) Over ½in. and under 2in in size,	say 5lbs.	25
(b) Over ¼in. and under ½in. in size,	say 3lbs.	15
(c) Over ⅛in. and under ¼in. in size,	say 4lbs.	20
(d) Under ⅛in. in size . ..	say 8lbs.	40
	20lbs.	100

It will be evident that one should not expect to find the heat value of all these grades similar. This will particularly apply when comparing the ½in. to 2in. sample with the under ⅛in. sample. In some cases the fine coal contains more heat units than the larger coal, but in the majority of cases the fine contains a large amount of dirt, and consequently is of lower value.

These heaps can be now further reduced, dealing first with the very fine. After thoroughly mixing, carefully weigh out 25 per cent. and place in a labelled covered tin. The remaining heaps of the larger grades should then each in turn be thoroughly ground and mixed. This can best be done by means of a " Spong No. 5 " Coffee Mill. Each grade should be treated separately, and, after grinding, passed through the ⅛in. mesh sieve. Twenty-five per cent. by weight of each should then be taken and placed in a separate labelled tin in the same way as the fine coal.

We should now have four tins containing a total weight of 5lbs. of coal, and are sure, so far, of having a proportionate amount of the better and inferior (large and small) coal This we could not have been so sure of had we ground the whole 20lbs., mixed it, and then taken out 5lbs.

Final Samples.

The next step is a still further reduction of the sample for analysis. Taking the first tin —This should all be ground to pass through a sieve having 30 meshes to the inch, thoroughly mixed, and 25 per cent of the total taken and placed in a covered tin. The other tins should then be treated in a similar manner separately; 25 per cent. of each, after having been passed through the 30 mesh to the inch sieve, to be added to the first sample. We are now certain of having one-sixteenth of the various grades of coal which were delivered to the laboratory in the original sample.

The next step is to thoroughly mix this remaining sample, and after taking a fair quantity of this for moisture determination—to be added to the amount already determined by air drying—take about a quarter of it, and with the use of a pestle and mortar *pass the whole of this quarter* through a sieve having 60 meshes to the inch. As with some coals, a loss of about ·5 per cent. occurs through dealing with small quantities at a time with the pestle and mortar in passing this sample through 1/60in. mesh, it is advisable to determine the moisture content on part of the sample before passing through the 1/60in. mesh. In any case this will be a check with moisture determination in the final sample.

Too much importance cannot be attached to seeing that the *whole* of this final sample passes through the sieve, for the more friable particles—which usually consist of clean coal—will more readily break up and pass through the fine meshes, leaving the harder particles—generally shale—behind; and if these are not broken to the same fineness and mixed with the remainder, the sample will be spoilt.

After thoroughly mixing this very fine coal on a sheet of glazed paper, we can take our samples, which must, of course, first be dried, for the Calorimeter Test and Analysis, from any part of the heap, and if the difference obtained from such samples exceeds ·2 per cent. for the former or ·1 per cent. for the latter, something must be wrong with the operation of determining the heat value or analysis, and the error should be looked for in this direction.

Although this operation of sampling may suggest loss of moisture during the whole period, on actual tests this loss has not exceeded ·5 per cent. even on a coal containing as much as 12 per cent. of hygroscopic moisture, and the smaller the quantity of hygroscopic moisture contained in a coal, the less chance there is of losing any moisture by this method. The maximum loss of ·5 per cent. on a coal of 12,000 B Th.U.'s amounts to 60 B.Th.U.'s, which is negligible when compared with the much greater error which can be introduced by incorrect sampling. Further, one has to remember that there will frequently be a loss of moisture during the original sampling before the coal reaches the laboratory.

THE LANCASHIRE & CHESHIRE COAL RESEARCH ASSOCIATION

THE INFLUENCE OF THE ADDITION OF INERT MATTER UPON THE VOLATILE MATTER EVOLVED WHEN COAL IS HEATED

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PREFACE

The object of the Research Association is to place at the disposal of the Lancashire Coal Industry the maximum amount of scientific information, either original or eclectic.

In our instructions to the Director of Research, we have emphasised the fact that the results of research carried out in our laboratories should be published as early as possible, consistent with accuracy. In consequence, some bulletins may appear somewhat incomplete, but as most of the research is to be continued, further results will be published as they are obtained.

It is not our intention to allow work to accumulate, and publish it in lengthy reports or papers, but to place useful and reliable information before the industry quickly in a convenient form.

We welcome any suggestions or criticisms on the publications, which should be addressed to F. S. Sinnatt, College of Technology, Manchester.

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THE INFLUENCE OF THE ADDITION OF INERT MATTER UPON THE VOLATILE MATTER EVOLVED WHEN COAL IS HEATED

Apart from the ultimate analysis, the determination of calorific value, the agglutinating value, and the results obtained by treating coal with solvents, comparatively few tests are available which enable the analyst to gain an insight into the properties of coal. It is suggested that the curves obtained by the method described in this bulletin may serve as an additional "characteristic" for coal. The results of the study may also be of some interest in connection with the subject of the stone dusting of mines, as indicating that the percentage of volatile matter which a coal evolves under the conditions of the ordinary volatile matter test, may not be a measure of the amount which the coal will evolve when mixed with inert matter (stone dust).

Introduction.

The influence of the following factors upon the percentage of volatile organic matter evolved when coal is heated has been studied:

I. The degree of fineness of the coal.

II. The addition of inert matter of varying degrees of fineness.

III. The addition of inert matter to coal in varying proportions.

Literature.

According to Somermeier (J Am. Chem. Soc., 1916, **26**, 1,002), the percentage of volatile matter given off is greater with large coal than when the coal is ground to a finer state of division, and, in his paper, the following results are quoted :—

TABLE 1.

	Moisture.	Volatile Matter. per cent
1/4—1/10	1·15	39·05
1/10—1/20	1·45	38·80
1/20—1/40	1·70	38·55
1/40—1/80	1·90	38·05
1/80 and finer	2·05	35·54

He states "that finer ground samples give somewhat lower volatile matter than coarse samples."

Some doubt having arisen as to whether these statements were true for all coals, especially for caking coals, the following experiments were carried out, using various caking coals, and it will be seen that with an increasing degree of fineness of the coal, there is a slight tendency for an increased percentage of volatile matter to be evolved. The figures are quoted in order to clear the ground for the matter which follows, but it will be observed that the influence of this factor upon the volatile matter evolved is not so pronounced as that caused by the addition of inert matter to the coal, as shown in the later part of this bulletin.

1. *The Influence of the degree of fineness of the coal.*

Three separate samples of coal, from three distinct seams, were selected, with the special object of eliminating any disturbing elements in the form of inert matter. The coals possessed the property of grinding homogeneously, *i.e.*, the coal and the ash pulverize at approximately the same rate. It may be pointed out that the error introduced by the influence of the ash upon the determination of the volatile organic matter is smaller than the experimental error, and consequently the coal may be considered to be free from external influences, which might detract from the accuracy of the results obtained in the experiments.

The proximate analyses were as follows :—

TABLE 2.

Percentage.	No 1 Coal. per cent.	No. 2 Coal. per cent.	No. 3 Coal. per cent.
Moisture	1·1	2·0	2·7
Ash.	3·2	5·1	3·6
Volatile Matter	33·3	33·5	26·5
Volatile Organic Matter.	32·2	31·5	23·8
Coke	66·7	66·5	73·5
Fixed Carbon	63·5	61·4	69·9

Two pounds of an average sample of each of the coals was ground to pass through a sieve of 1/10 mesh, the whole of the sample being made to pass through the sieve; it was then intimately mixed and divided into five equal portions. The first portion was re-sieved, and that which passed through a 1/30 sieve eliminated. During the grinding every attempt was made to crush the coal in such a manner that a minimum amount only passed through the sieve having the finer mesh. The whole of the particular portion was treated in this manner. Determinations of the ash in the material passing through the sieve of smaller mesh showed that there was practically no change in the percentage of ash present. Each of the five portions was treated in a similar manner, for each succeeding tier of sieves, the sizes taken being 1/10—1/30; 1/30—1/60; 1/60—1/90; 1/100—1/200, and through 1/200. The volatile matter was then estimated in each of the separate portions, with the results shown below. :—

TABLE 3

Portion.	Degree of Fineness of Coal.	No. 1 Volatile Organic Matter. per cent	No. 2 Volatile Organic Matter. per cent.	No. 3 Volatile Organic Matter. per cent.
1	1/10—1/30	32·2	31·2	24·1
2	1/30—1/60	32·2	31·5	24·2
3	1/60—1/90	32·5	31·3	25·1
4	1/100—1/200	32·9	31·6	24·9
5	1/200 & finer	33·4	32·0	26·3

(Volatile organic matter or volatile combustible matter is obtained by deducting the percentage of moisture from the volatile matter.)

From the above results, it would appear that there is a slight increase in the percentage of volatile organic matter evolved, the finer the state of division of the coal.

It may be observed that the conditions under which the experiments were carried out were made as standard as possible, attention being paid to the following details, which are liable to variation. The calorific value of the gas was constant; the same platinum crucible and bunsen was used in all the tests, and the bench on which the experiments were carried out was completely sheltered from draughts.

The method adopted was that of the American Coal Committee (J. Am. Chem. Soc., 1899, 21, 1,119). One gram of the coal was placed in a platinum crucible weighing 20 or 30 grams, and having a tightly fitting cover. It was heated over a full bunsen flame (8in. high) for exactly seven minutes, allowed to cool in a desiccator, and re-weighed. Repeated determinations carried out in blank experiments showed the temperature of the coal in the crucible to be 700° C. to 705° C. at the beginning of the test, and 720° C. to 728° C. at the end of seven minutes' heating. The temperature was ascertained by means of a standardised platinum platinum-rhodium couple, in conjunction with a portable indicator made by the Cambridge Scientific Instrument Company.

2. *The addition of inert matter of varying degrees of fineness.*

The influence of varying the size of the inert matter used upon the percentage of volatile matter evolved was determined in one specimen of coal. One unit of coal powdered to pass through a 1/60 sieve, and be caught by a 1/90 mesh sieve, was mixed with four units of inert matter (electrode carbon) of varying degrees of fineness. One gram of the resulting mixture was then carbonised.

TABLE 4.

Size of Inert Matter (electrode carbon).	*Percentage of Volatile Organic Matter Evolved, calculated on coal taken.
1/10—1/30	28·6
1/30—1/60	29·0
1/60—1/90	29·4
1/100—1/200	29·4
1/200 and finer	29·6

* Mean of three determinations for each experiment.

3. *The addition of inert matter to coal in varying proportions.*

It appeared necessary to carry out the above experiments in order to show that the degree of fineness of the coal, and of the inert matter, did not interfere with the results obtained during the determination of volatile organic matter.

The main object of the paper is to examine the influence of the addition of inert matter upon the volatile organic matter evolved, when coal is heated. In order to ensure that this was the only factor in operation in all the experiments, each sample of coal was graded to the same degree of fineness, namely, to pass through 1/60 and be caught by a 1/90 sieve. In the first place three distinct types of inert matter were experimented with—pure white Calais sand, in order to test the influence of silicious material; coal ash, obtained from the same coal upon which the experiments were carried out; electrode carbon, which, when experimented upon under the conditions of the usual volatile organic matter test, yielded no volatile organic products.

One unit weight of coal was intimately mixed with varying multiples of its weight of inert matter, which had been powdered to pass through a 1/60 sieve, and be caught by a 1/90 sieve. One gram of the resulting mixture was heated under the standard conditions described earlier in the paper. The percentage of volatile organic matter evolved from the coal was then determined.

The first specimen of coal examined was Arley (Wigan).

TABLE 5.

Ratio of inert matter (electrode carbon) to coal.	Percentage of volatile organic matter evolved, calculated on weight of coal.
0	31·2
1	32·3
2	32·9
3	33·7
4	35·6
5	35·9
6	36·5
7	36·9
8	38·7
9	39·7
12	40·2
16	40·8
20	41·0

TABLE 6.

Ratio of inert matter (White sand) to coal.	Percentage of volatile organic matter evolved, calculated on weight of coal.
0	31·2
1	34·1
4	35·3
8	37·2
10	38·7
12	38·6
16	39·1
20	39·6

TABLE 7.

Ratio of inert matter (coal ash) to coal.	Percentage of volatile organic matter evolved, calculated on weight of coal.
0	31·2
1	33·7
4	37·2
9	38·6

The above results are plotted in the curves shown in Fig. 1.

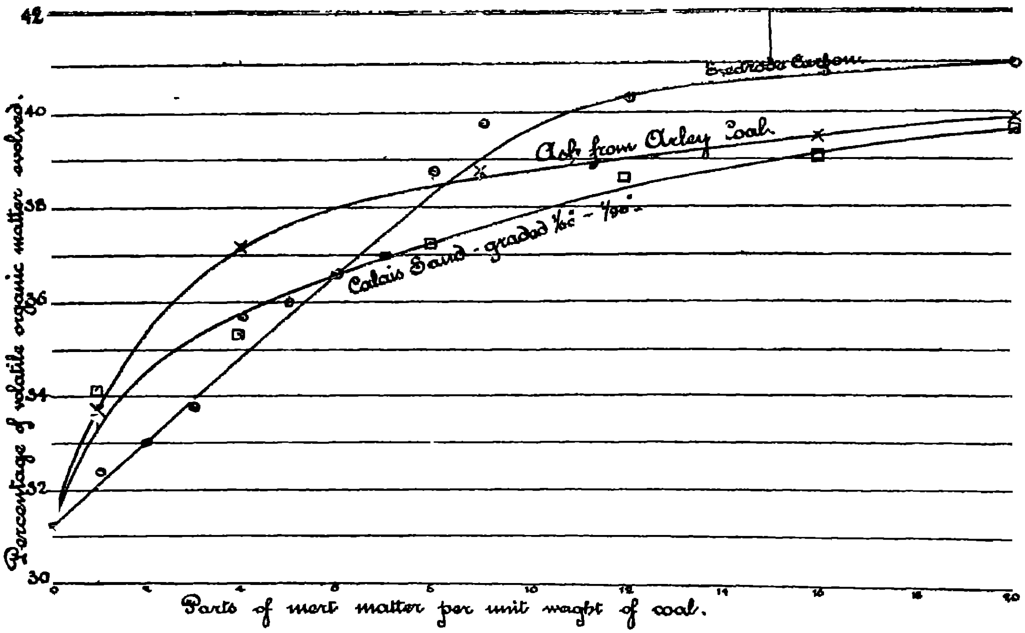
Percentage of volatile organic matter evolved.
42
40
38
36
34
32
30
Electrode Carbon
Ash from Arley Coal.
Calais Sand - graded 1/60" - 1/90"
0
2
4
6
8
10
12
14
16
18
20
Parts of inert matter per unit weight of coal.

Fig. 1.

TABLE 8.

COAL.	WEIGHT OF ELECTRODE CARBON PER UNIT WEIGHT OF COAL ..	0	4	8	12	16	20
Arley. (No. 7, Fig. III.)	Percentage volatile organic matter, calculated on weight of coal	31·2	35·6	38·7	40·2	40·8	41·0
	Increase in percentage of volatile organic matter	—	4·4	3·1	1·5	0·6	0·2
Bacon Mine. (No 1, Fig. II.)	Percentage volatile organic matter, calculated on weight of coal	38·0	40·1	46·4	50·6	50·6	50·0
	Increase in percentage of volatile organic matter	—	2·1	6·3	4·2	—	—
Garswood, 9ft. (No. 5, Fig. III.)	Percentage volatile organic matter, calculated on weight of coal	35·3	38·0	40·0	44·0	46·5	46·4
	Increase in percentage of volatile organic matter	—	2·7	2·0	4·0	2·5	—
Hell Hole. (No. 6, Fig. III.)	Percentage volatile organic matter, calculated on weight of coal	33·9	36·5	40·0	42·0	43·0	43·2
	Increase in percentage of volatile organic matter	—	2·6	3·5	2·0	1·0	0·2
Lower Mountain Mine. (No. 4, Fig. II)	Percentage volatile organic matter, calculated on weight of coal	27·3	31·1	31·6	32·0	32·8	32·3
	Increase in percentage of volatile organic matter	—	3·8	0·5	0·4	0·8	—
Pemberton, 2ft. (No 3, Fig. II.)	Percentage volatile organic matter, calculated on weight of coal	34·8	36·3	41·0	42·3	42·6	43·0
	Increase in percentage of volatile organic matter	—	1·5	4·7	1·3	0·3	0 4
Ravine. (No. 2, Fig. II.)	Percentage volatile organic matter, calculated on weight of coal	31·7	36 6	42·2	43·7	44·3	45·3
	Increase in percentage of volatile organic matter	—	4·9	5·6	1·5	0·6	1·0
Hoo Cannel. (No. 8, Fig. III.)	Percentage volatile organic matter, calculated on weight of coal	28·0	28·6	29·6	29·6	30·4	30·0
	Increase in percentage of volatile organic matter	—	0·6	1·0	—	0·8	—

It will be observed that there is a distinct increase in the volatile matter evolved, with an increase in the proportion of inert material present, but that the rate of increase is evidently not modified greatly by altering the inert matter. In view of this fact it was decided to use electrode carbon in the subsequent experiments; electrode carbon possesses distinct advantages over Calais sand, in that its specific gravity is about half that of sand, it is easy to procure, and lends itself to grinding and grading to any desired degree of fineness. Further, it contains no volatile constituents, except 0·17 per cent. of moisture, which remains constant.

Eight seams, representative of Lancashire coals, were examined to determine the relative increase in volatile organic matter, which occurred when the coals were mixed with varying proportions of inert matter (electrode carbon). The coals were treated in the manner described for Arley coal, and the results are shown in Table 8.

The results are plotted in the curves shown in Figs. 2 and 3.

The maximum increase in volatile organic matter has been calculated upon a basis of the volatile organic matter found in the pure coal. The results are given below :—

TABLE 9.

Coal.	Maximum increase in volatile matter per cent.
Arley	31·4
Bacon Mine	33·2
Garswood, 9ft.	31·7
Hell Hole	27·4
Mountain Mine	18·3
Pemberton, 2ft.	23·5
Ravine	42·9
Hoo Cannel	8·6

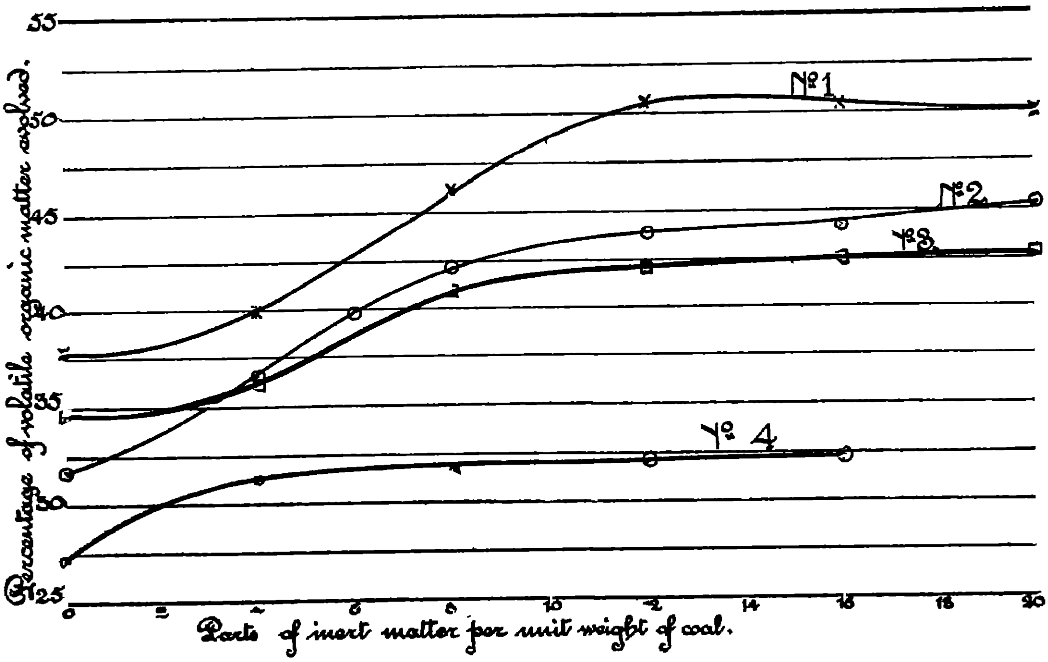55
50
45
40
35
30
25
Percentage of volatile organic matter evolved.
0
2
4
6
8
10
12
14
16
18
20
Parts of inert matter per unit weight of coal.
Nº1
Nº2
Nº3
Nº 4

Fig. 2.

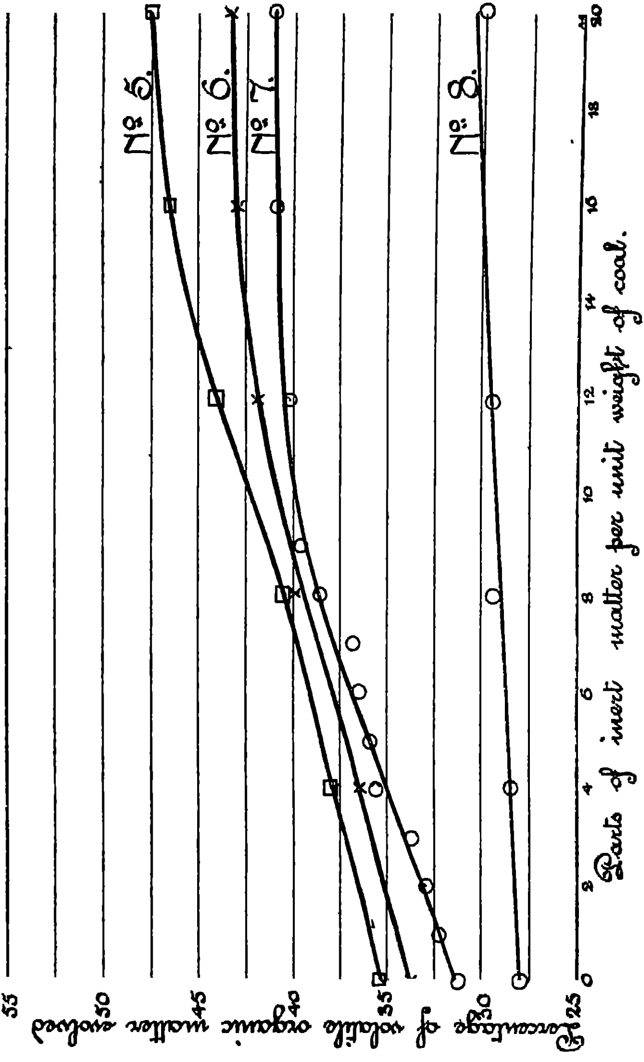
Percentage of volatile organic matter evolved
25
30
35
40
45
50
55
Parts of inert matter per unit weight of coal.
0
2
4
6
8
10
12
14
16
18
20
Nº 5.
Nº 6.
Nº 7.
Nº 8.

Fig. 3.

It will be seen from these figures that the coals vary considerably in this respect, and it is to this point that particular attention is drawn. It is usually stated that the percentage of volatile matter present in mine dusts is an important factor in the liability of the dusts to explosion. The experiments described show that the volatile matter produced when coal is heated increases appreciably if the coal is mixed with inert matter. The following example shows the nature of the increase to be expected. One unit of Ravine coal (31·7 per cent. volatile organic matter) mixed with four units of inert matter should, by calculation, yield a mixture capable of evolving 6·3 per cent. of volatile organic matter. According to the determination, the actual amount evolved was 7·3 per cent. of volatile organic matter. It is clear that evidence is required to show how this applies to the mixture of coal and stone dust (inert matter) existing in mines. Stone dust contains a certain percentage of matter which is evolved on heating, and this introduces factors into the problem which may make a more prolonged study desirable. It was decided to place the experiments on record, in order to open up the subject to any who may be interested. It is proposed to continue the work, and to examine the action of certain stone dusts used in Lancashire collieries, upon the percentage of volatile organic matter evolved when coal is heated.

The results may also be of interest from the point of view of the test used for the determination of the agglutinating value of caking coals. This test consists in determining the maximum amount of inert matter (sand, anthracite, &c.) with which coal can be mixed, and still yield a coherent button of coke. A special bulletin will be devoted to this problem.

It is also considered that the work may have some bearing upon the efficiency claimed for the process of mixing coke and coal for steam-raising purposes. In such a mixture the coke would act as an inert substance. Such a result would be of special value where the only available coal is one having a highly caking nature, in which case dilution with coke would have two distinct results, namely, to decrease the coherence of the coke produced from the coal, and, secondly, to increase the percentage of volatile matter given off.

The attempt to find an explanation of the observations recorded is left until further experimental evidence has accumulated.

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

NOTES ON
COAL ANALYSIS

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PRICE
TWO SHILLINGS

BULLETIN 4
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PREFACE

It is a matter of some regret that we are compelled to look to America for standardised methods for the valuation of coal; it is well known that much of the original work on the subject has been done in this country.

The present bulletin on Coal Analysis was prepared for the information of the members of the Coal Research Association, but it is thought that it may be of value to others interested in the valuation of coal.

The time appears to be opportune for placing the purchase of coal upon a scientific foundation, but this will not be possible until consumers, merchants, and collieries have agreed upon the methods of valuation most suited to the general conditions under which coal is consumed.

Suggestions and criticisms will be welcomed and acknowledged in any further edition.

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INTRODUCTION

The chemical analysis of coal serves two broad purposes. first, to determine the relative merits of coals, the properties of which have been proved to be suited to a particular industrial purpose; and, secondly, as a preliminary to the investigation designed to ascertain the best possible method of utilising any particular seam In an enlightened policy of coal conservation it would not be possible for seams which are ideal for use in, say, vertical retorts for the manufacture of coal gas to be sold for domestic fires, and for coals, rich in nitrogen, to be wasted in furnaces simply because no complete investigations of the properties of the coals have been published. The chemical analysis of the mother substance of the coal should be accompanied by an enquiry into the geological environment of the coal, an examination of the structure microscopically, and by the performance of as many tests as possible devised to exhibit any special characteristics of the mother substance.

In the past the chemist has been prone to attempt to interpret the results of the chemical analysis in terms of properties of the coal with which the values have no direct relationship. When it is remembered that such a vital characteristic as the caking property may be completely destroyed by mild oxidation of the coal, and that the amount of oxygen which is responsible for the change, cannot be accurately determined by analysis, the difficulty of interpreting the analytical values will be realised. A highly caking and a non-caking coal may in fact yield the same values on analysis, or in other words the two coals may be said to be isomeric.

The Chemical Analysis of Coal.

The chemical analysis of coal is generally considered in two parts, viz., the approximate (proximate) and the ultimate analysis. The former includes four determinations—the moisture, ash, coking value and the calorific value—and the results enable the analyst to make a fairly accurate estimate of the comparative values of samples of coal, or to control the variations in quality of a particular supply. The analysis may be completed in about two hours, and on this account the results are of considerable commercial importance. The work can be done by an untrained man, and the apparatus required is inexpensive.

In the "Electrical Review" for 5th December, 1919, 709, J. Devlin states that the approximate analysis of coal, including the following determinations, moisture, ash, volatile matter and calorific value by a bomb calorimeter, is successfully performed by an ex-soldier with one arm.

The services of a chemist are required for the ultimate analysis, and the time necessary for its completion depends upon the purposes for which it is needed. The ordinary routine analysis generally takes about three days.

COAL ANALYSIS

Percentage of Small Coal.

During the process of sampling and before the coal has been crushed, one of the portions rejected during quartering should be preserved and the percentage of small coal present determined. One half to one hundredweight is sieved and the fine coal separated and weighed; a portion is also taken for analysis. The size of the mesh of the sieve will depend upon the size of coal under examination, but the measurements given below will be found to be suitable. This test indicates the proportion of small coal present in the consignment; it also forms one of the simplest checks on any further deliveries. If the percentage of fine coal differs widely from that present in the original sample, then variation in the quality may be expected.

In the Standard Coal Specification (Coal and Iron Trades' Review, 28th March, 1913), there is a clause specifying the limiting percentage of small coal permitted in deliveries of coal. The methods of testing are indicated in the following table, showing the requirements for bituminous coals, washed and dry screened from Durham and Yorkshire.

Dry Screened Coals.	Moisture. Per cent.	Size of Square Mesh.	Percentage of Small Coal passing through.
1. Double Nuts 12,750 B.T.U.	5	½in.	17½
2. Single Nuts 12,500 B.T.U.	6	⅜in.	25
3. Peas 12,250 B.T.U.	6	¼in.	25

Washed Coals	Moisture. Per cent.	Size of Square Mesh.	Percentage of Small Coal passing through.
1. Washed Double Nuts 13,250 B.T U.	8	½in.	15
2. Washed Single Nuts 13,000 B.T.U	9	⅜in.	17½
3. Washed Peas 12,750 B.T.U.	10	¼in.	20

The Sampling of Coal.

The method of obtaining an average sample of coal is described in "The Sampling of Coal" (Bulletin 2, Lancashire and Cheshire Coal Research Association)

The sample for the approximate analysis should have been crushed to pass through a sieve of $\frac{1}{40}$ or $\frac{1}{80}$ mesh, and should be air dried. It is necessary to determine the moisture in the coal before it is air-dried, in order to ascertain the amount actually present in the coal from which the sample was derived. It is difficult to preserve coal, even in a sealed vessel for any length of time without marked variations taking place in the moisture content unless a store at a perfectly uniform temperature is available; during ordinary storage the moisture from the coal will frequently be found deposited on the walls of the containing vessel. The amount of moisture present in coal may be standardised by air-drying, *i.e.*, exposing it freely to the air in a thin layer for a period of not less than 24 hours. An essential factor of the term "air-dried" should be a statement of the humidity of the air during the whole period of the exposure, or at least during the last six hours.

A number of experiments have been carried out by Burrows Moore and the author, to ascertain the exact relationship existing between the moisture content of coal, and the humidity of the air. The following figures are quoted to illustrate the fact that the percentage of moisture present in coal varies directly with the degree of humidity of the air, and that variations, caused by a change in humidity influence the moisture present in the coal in a few hours. It will be observed that the variations in the moisture present are as great as 0·5 per cent. in about six hours.

Coal.	Mesh.	Time.	Moisture. per cent.	Degree of Humidity
Arley (Wigan) ..	1/30 ..	9-46 a.m. ..	2·19 ..	88·0
,, ..	,, ..	7-0 p.m. ..	2·08 ..	73·0
,, ..	1/180 ..	9-46 a.m. ..	3·03 ..	88·0
,, ..	,, ..	7-0 p.m. ..	2·56 ..	73·0
Indian	1/30 ..	10-40 a.m. ..	4·30 ..	73·5
,, ...	,, ..	3-50 p.m. ..	4·75 ..	79·5
,, ...	1/200 ..	10-40 a.m. ..	4·36 ..	73·5
,, ...	,, ..	3-50 p.m. ..	4·76 ..	79·5
Peat	1/30 ..	9-20 a.m. ..	14·40 ..	68·8
,, ...	,, ..	3-45 p m. ..	13·75 ..	63·6
,, ...	1/200 ..	9-20 a.m. ..	13·60 ..	68·8
,, ...	,, ..	3-45 p m. ..	13·04 ..	63·6

Wigan Arley is a caking bituminous coal.

Indian is a bituminous coal having little caking power.

The *Peat* is an ordinary English variety.

When a particular type of coal is being examined frequently, it is desirable to prepare a graph showing the percentage of moisture in the coal for varying degrees of humidity of the air.

Special precautions are described in the Report on an Investigation of the Coals of Canada, 1912 (Vol. II.).

Approximate Analysis of Coal.

Three chemical determinations are included under the heading the "Approximate Analysis of Coal," namely, the moisture, ash, and the coke or volatile matter.

Moisture in Coal.

As it is not practicable to use coal of a coarseness of $\frac{1}{40}$ or $\frac{1}{60}$ mesh for certain of the determinations in the ultimate analysis, a finer state of division is required. As a rule, the coal should be ground to pass through a sieve of about $\frac{1}{90}$ to $\frac{1}{100}$

mesh in a coffee-mill grinder, or in a porcelain ball mill, and when this is necessary, a further determination of moisture on the fine material should be made. A correction may then be applied for the loss of moisture which has occurred during the fine grinding. According to P. Nicolardot, International Congress of Applied Chemistry, 1912, the loss from this cause is negligible. In Bulletin 323 of the Geological Survey, U S.A., there is a careful study of the loss of moisture by coal (*a*) when exposed to air under varying conditions, (*b*) when different methods of pulverising are used, (*c*) when varying weights of coal are used for the determination of moisture. Fieldner (Chem. Engineer, 1913, 17, 50) states that only a difference of 0·15 per cent. in moisture content was found between air-dried coal ground to pass through a ¼in. mesh, and that ground in a ball mill to pass through a 1/60 mesh.

It is important to recognise that the whole of the figures obtained in the coal analysis depend upon the value obtained in this determination, and the greatest care should be exercised to ensure the standardisation of the method adopted. The results affect directly the percentage of hydrogen found in the coal; if the percentage of moisture as estimated is lower than that actually present in the coal, the percentage of hydrogen found during the determination by combustion will be correspondingly higher.

As coal does not become constant in weight when heated, an empirical process for the determination of moisture is generally adopted for ordinary routine purposes; the following method will be found convenient.

Method. One gram of coal is spread over a watch-glass or shallow flat-bottomed dish, and heated in an oven at 105° C. for one hour. It is then covered, transferred to a desiccator and allowed to cool. It should not remain in the desiccator any longer than is required to cool completely (20 minutes); the subsequent weighing must be carried out as rapidly as possible. The loss in weight is assumed to be the moisture present in the coal.

The results obtained by this method do not represent the actual moisture present in the coal, as the change in weight which occurs includes the following: (1) Decrease due to loss of water, evolution of occluded gases, and slight decomposition of the coal. (2) Increase during the final weighing, owing to absorption of moisture from the air, and slight oxidation which is taking place throughout the determination.

The results are more constant if the oven is fitted with the means for changing the air in it about three times a minute. The air should be dried by passing it through concentrated sulphuric acid (Jour. Ind. Eng. Chem. 1917, *9*. 100)

The following table, quoted by Douglas (Gas World, 1912, 415), shows the changes which may occur when coal is heated to various temperatures :—

	Grams.
Coal dried at 100° C	5 0000
After 1 hour at 130° C.	4 9816
,, ½ ,, 150° C.	5·0094
,, ½ ,, 175° C.	5·0346
,, 6 ,, 175° C .. .	5 2036
,, 3 ,, 200° C.	5 2654
,, 3 ,, 200° C.	5·2186

It will be observed that the coal reaches a maximum gain in weight of about 5·3 per cent, and was found to have lost its power of yielding coherent coke, indicating a distinct chemical change in the coal substance. Experiments upon the loss of moisture by bituminous coals and anthracites are described by Archibald and Lawrence (Jour. Ind. Eng. Chem., 1912, *4*, 258), who show that the official process of the United States (heating for one hour at 105° C.) yields low results. In the case of certain special bituminous coals, the error was found to be 40 per cent. of the true moisture content. These experimenters believe the cause to be due to the oxidation of sulphur compounds, and to incomplete expulsion of moisture. They recommend heating the coal to at least 110° C. in a current of dry air, and collecting the moisture in a weighed calcium tube. (See p. 10.)

It is known that coals containing clay do not evolve the whole of the moisture present when heated to 130° C., as the water is present as part of the constitution of the clays. Certain coal ashes appear to have a composition identical with dehydrated kaolin, which normally would contain about 8 to 13 per cent. of water, whilst shales, which occur as impurities in coal, frequently contain up to 13 per cent. of water of constitution.

Method. A method for the determination of moisture in coal, which yields more accurate results, is as follows :—

The coal is placed in a platinum or porcelain boat, and heated in a tube surrounded by a bath of glycerin and water (50 per cent.) at about 110° C ; dry air, coal gas, or nitrogen, is passed over the coal and then through a weighed calcium chloride tube. At the end of the experiment the calcium chloride tube is reweighed, and the increase represents the moisture present in the coal. It has been found that from two to three hours are required for the expulsion of the moisture. One form of the apparatus used is shown in Fig. 1.

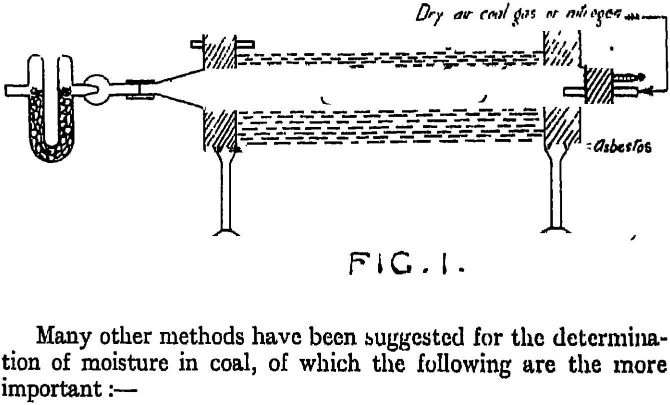

FIG. 1.

Many other methods have been suggested for the determination of moisture in coal, of which the following are the more important :—

A known weight of the coal is placed in a vacuum desiccator containing concentrated sulphuric acid for 24 hours. The loss in weight is assumed to be the moisture present in the coal.

A considerable weight of the coal is distilled in a Hoffman's apparatus, with toluene or xylene; the latter is condensed, collected in a special receiver, and the water which separates is measured.

A known weight of the coal is heated to 105° C. in a vacuum, the loss in weight being taken as the water present.

Determination of Ash.

It is frequently stated that the residue from the determination of moisture should be taken for the estimation of ash. This is not desirable, as it leads to an unnecessary waste of time; the determinations of ash, moisture, and coking value, should be carried out simultaneously.

Method. Three to five grams of air-dried coal are placed in a silica dish (2in. diam. by ½in.), or in a platinum capsule. The dish and contents are heated slowly over a small Bunsen flame, until the main proportion of the volatile matter has been driven off. The dish is then transferred to a gas or electrically-heated muffle, the temperature of which should be uniform. It is allowed to remain until completely free from organic matter, and is placed in a desiccator until cool and re-weighed. The amount of residue is the ash in the coal.

Alternative Method. One to two grams of coal are placed in a porcelain, silica or platinum boat. This is brought into a short length of combustion tubing (silica), one end of which is connected with an aspirating pump, and the other open to the air. The coal is first gently heated, and then more strongly, air being aspirated through the tube. If required, a slow stream of oxygen may be passed over the coal during the ignition, which greatly increases the rate of combustion. The supply of air or oxygen must be very carefully controlled, until the volatile constituents have been evolved, as there is a danger of fine particles of ash being carried out of the boat in the stream of gas. When the organic matter has completely disappeared, the boat and its contents are allowed to cool in a desiccator, and re-weighed. The method is more rapid than heating over a Bunsen, but slower than when a muffle is available. It possesses the distinct advantage that the ash does not come into contact with the products of combustion of the gas.

F. Weisser (Chem. Zeit., 1914, *38,* 1264 and 1289) states that the results obtained by heating over a Bunsen are the more accurate, as the loss due to decomposition of carbonates is compensated for by absorption of sulphur dioxide produced from the gas, whilst H. Mastbaum (Chem. Zeit., 1918, *42,* 385-386, and 391-392) states that ignition over a Bunsen yields higher results than when a muffle is used, as sulphur compounds of gas are absorbed by calcium or other carbonates or oxides in the ash.

In the above methods, the preliminary heating is to prevent the spurting which may occur during the rapid evolution of the volatile matter and moisture. It also causes a low temperature carbonisation coke to be formed, which is not so difficult to oxidise as one produced at a high temperature. It is seldom possible to obtain a constant weight after a second ignition, owing to the slow decomposition and modification of the inorganic compounds contained in the ash, and consequently it is important that the temperature to which the coal is heated should be constant. It has been found that a temperature of about 800° C. is a suitable one for the muffle. As a rule, coal ash will not fuse at this temperature, and thus the possibility of particles of unburned organic matter remaining in the centre of the fused masses is avoided. Further, it prevents the rapid divitrification of the silica ware dishes, which takes place at higher temperatures. When the organic matter in the fuel is found to oxidise with difficulty—as is the case with certain classes of coke and anthracite—the fuel should be very finely pulverised, and spread over the bottom of the dish, by means of a few drops of ash-free alcohol.

It is obvious that the ash obtained is not the actual inorganic substance present in the coal, as during the ignition most of the compounds present undergo complete or partial decomposition. It is for this reason that a standard temperature should be adopted, as it has been shown that considerable variations in the composition of the ash may be brought about by altering the temperature of ignition. Differences as high as 1 per cent.

in the ash content have been obtained between a low temperature and a bright red heat This is noticeable when the coal is rich in carbonates and sulphides, and applies especially when the percentage of ash is high.

Analysis of the Ash.

Ash to be used for the chemical analysis should be obtained by ignition of the coal under conditions which preclude the possibility of its contact with the products of combustion of the gas. Either gas free from sulphur compounds, the second method described on p. 11, or an electric furnace must be used for the ignition. There is also a possibility that a loss of potassium may occur, and where this element is being determined, the coal should be treated with nitric and sulphuric acid, and evaporated to dryness before incineration (J. Ind. and Eng. Chem., 1917, *2*, 753). The constituents of the ash are then converted into sulphates.

It is not proposed to describe in detail methods for the analysis of the ash, as these can be found in text-books on chemical analysis. The following is a summary of the procedure :—

The finely pulverised ash is fused in a platinum crucible with a fusion mixture of sodium and potassium carbonates. When the ignition is complete, the fused mass is washed out of the crucible with water, hydrochloric acid added, evaporated to dryness twice, and the residue heated to 110° C. for one hour. The mass is treated with dilute hydrochloric acid, and the silica is removed by filtration; the latter is treated in the usual manner, and determined. The filtrate is diluted to a known volume and an aliquot portion is used for the determination of iron, aluminium, manganese, calcium, and magnesium. Further portions are taken for the estimation of the phosphates and other acid-radicles present. A fresh portion of the ash is fused with calcium carbonate or pure lime (Lawrence Smith's method) for the estimation of potassium and sodium.

The following are some typical analyses of coal ashes (chiefly from J. T Dunn, J.S.C.I , 1918, 37, 16T) :—

Percentage Composition.

								Coals freed from ankerites.*		
Silica	. 25 90	40·40	45·40	47·10	51·80	51·15	51·89	32·9	27·7	30·2
Alumina	.. 17·46	29 34	35·53	37·39	38·25	44·70	44·59	26·8	19·8	30·4
Ferric Oxide ..	.. 16·86	15·21	12 57	11·14	5·64	1·25	0·98	23·3	38 4	21·4
Manganese Oxide ..	.. trace	0·30	none	0·40	trace	trace	none	trace	trace	trace
Lime	.. 22·80	4·61	3·54	0·82	0 45	0·15	0·38	6·8	8·6	7·7
Magnesia	.. 3·22	1·96	1·23	0·65	0·74	0·36	0·38	3·1	2·3	4·0
Alkali	.. 2·70d	7·23	0·83	1·38	1·71	1·20d	1·77	3·8	0 8	1·1
Titanium Oxide ..	.. 0·74	0·95	0·90	1·12	1·41	1·15	0·15	—	—	—
Sulphuric Anhydride	.. 8·91	—	—	—	—	—	—	3·0	2·2	6·0
Phosphoric Anhydride	.. 1·55	—	—	—	—	—	—	—	0·3	0·2
Quicklime	.. 5·95	—	—	—	—	—	—	—	—	—
Fusion Temperature °C.	1020	1230	1380	1460	1500	—	—	—	—	—

* Bayley, Grounds & Sinnatt (unpublished work).

Inorganic Partings in Coal.

When coal contains inorganic partings a distinction should be drawn between the composition of these substances and the inorganic compounds present in the coal substance. If possible, the amount of parting present in the coal should be determined by breaking up a number of typical lumps and picking out the material by means of forceps, the substance should also be analysed separately. To illustrate the amount special coals may contain, one sample was examined and 3·0 per cent. of white parting found to be present; the total amount of ash in the coal was 4·2 per cent. The composition and properties of the ash of this coal depended to a large degree upon that of the white parting.

A number of the partings have been examined and the results will be published in a separate bulletin. The following is the composition of a typical example* :—

Ferrous oxide (FeO)	14·0 per cent.
Manganese oxide (MnO)	0·9 ,,
Calcium oxide (CaO) . .	42·1 ,,
Magnesium oxide (MgO)	Nil (generally present)
Carbon dioxide (CO_2)	42·2 per cent.
Sulphur trioxide	Nil.
Sulphur	0·4 per cent.

Corresponding to the following :—

Ferrous carbonate	22·5 per cent.
Manganese carbonate	1·5 ,,
Calcium carbonate	75·2 ,,
Pyrites (FeS_2)	0·7 ,,

The compound is a substituted calcium carbonate, and is of the type usually classed as an ankerite. The general term "ankerites" is a suitable one for the white partings.

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* Bayley, Grounds & Sinnatt (unpublished work)

The Fusibility of Ash.

The Determination of the Fusibility of Coal Ash. The following method is described by J. W. Cobb (J.S.C.I., 1904, *23*, 11). It is based on a method described by Le Chatelier and Chantetre (Bull. de la Soc. d'Encouragement, 1902, 102, *2*, 223). The ash is pulverised until it will pass through a sieve of 100 mesh to the inch, or finer. It is then made into a paste with water, and moulded into a pyramid with a square base, having one face vertical. The dimensions of the pyramid should be, base 1in., height 3in., or, if insufficient ash is available, the pyramid should have the same proportional size, but smaller dimensions. The pyramid is then thoroughly dried, and placed in a furnace or muffle, the temperature of which is gradually raised, until the pyramid begins to bend. At the first sign of bending, the heating of the furnace is moderated. The temperature at which the apex of the cone sinks until it is in the same plane as the base is assumed to be the temperature of fusion of the coal ash. The temperature of the furnace must be determined by some form of pyrometer, the most convenient being a thermo couple, but in the absence of this, a Watkin recorder, or Seger cone. Fieldner and Hall (J. Ind. and Eng. Chem., 1915, 7, 829) suggest that in preparing the ash the coal should be incinerated below 800° C., and the ash ground to pass through 1/200 mesh sieve, and made into a plastic with a 10 per cent. solution of dextrin. It is moulded into cones, 1in. high and $\frac{3}{16}$in. base, partially dried and mounted on a highly refractory base. It is then dried, and the temperature of fusion determined in an atmosphere of 50 per cent hydrogen and 50 per cent. steam in a special electric furnace.

The fusion point of coal ash is, as a rule, between 1,000° C. and 1,500° C., and in the table given below will be found the fusion point of coals having ashes of widely different composition. Palmenberg (J.S.C.I., 1913, p. 1144) gives the results of the examination of many samples of coal ash, which contained widely different percentages of iron. The results quoted in his paper make it clear that the presence of iron (ferric) has very little influence upon the temperature of fusion of coal ash, and that a direct determination of the fusing point of ash is essential, but Burgwin (J. Ind. and Eng. Chem., 1914, *6*, 694) does not agree that there is no relationship between the combined iron and sulphur contents of the coal and the fusing temperature, and points out that coals with more than 3 per cent. of iron and sulphur present (with few exceptions) give ashes melting below 1,400° C

Fusing Temperature of the ash in coal arranged according to the iron content

No.	Fe_2O_3 per cent.	Sulphur per cent	Ash per cent.	Fusion temp. Deg. F.
1	4·81	0·51	5·15	2700
5	7·94	1·52	15·61	2750
10	15·21	1·42	7·98	2400
15	19·19	1·79	7·90	2138
20	22·57	2·00	9·03	2336
25	27·22	3·13	13·54	2138
30	35·13	2·13	6·25	2300
35	39·88	2·41	8·96	2372
38	44·39	3·51	9·34	2318

Fieldner and Hall (J Ind. and Eng. Chem., 1915, 7, 299, 742, 829) show that the softening temperature is affected by the size and shape of the pyramids, the fineness of the ash, the rate of heating, and the way in which the pyramid is moulded; but the most important factor is the atmosphere in which the test is conducted. The variations may be up to 500° C. between carrying out the test in air, and in a partially reducing atmosphere; in the latter, ferric compounds are reduced to ferrous, which are active agents in slag formation, and in lowering the temperature of fusion.

Determination of the Carbonates (carbon dioxide) in Coal.

The determination of the percentage of carbon dioxide occurring as carbonates in coal is of interest from two aspects; it affords a criterion of the composition of the inorganic constituents, which, combined with the chemical analysis of the ash, makes it possible for a more accurate conjecture to be made of the composition of the inorganic compounds present, and, secondly, without the knowledge it is not possible for the determination of carbon to be corrected for the amount of carbon dioxide which is produced from the decomposition of the carbonates during the combustion process. It is not convenient to use an apparatus of the type of Schroetters, as the amount of carbon dioxide evolved is not sufficient. A method described by the author (Analyst, April, 1913) for the determination of carbon dioxide in carbonates has been successfully applied. The carbon dioxide evolved when the coal is treated with hydrochloric or phosphoric acid is collected in a dry, evacuated flask. The carbon dioxide is determined by the addition of standard barium hydrate solution, the excess of the latter being found by titration with standard hydrochloric acid. Typical results are given below* :—

	Per cent. of carbon dioxide.
Coal No. 1	0·67
„ No. 2	0·47
„ No. 3	0·90

Method of Determination of Volatile Matter and Coke.

The method most widely adopted is the original one suggested by the American Coal Committee.

Method. Exactly one gram of fresh, air-dried, powdered coal is placed in a platinum crucible (weight 20 to 30 grams) having a tightly-fitting lid. The crucible is supported on a platinum triangle (or thin silica) from 2½in. to 3in. above the top of a Bunsen burner, the flame of which should be 8in. high. The coal is heated for exactly seven minutes, after which the crucible is transferred to a desiccator, allowed to cool, and the loss in weight determined. This loss in weight is called the volatile matter, and the residue in the crucible is the percentage of coke.

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* Harrison & Sinnatt (unpublished work).

More concordant results will be obtained by using a Meker burner, and placing the crucible ½in. above it. Better results will be obtained by using either an electrically-heated furnace, or a gas-heated muffle, in place of either of the above sources of heat. The American Coal Committee (Jour. Ind. Eng. Chem., 1917, *9*, 100) describe a convenient form of electrically-heated furnace, which is the one to be adopted in future in American practice. It may be pointed out that the furnace is very similar in construction to the one described by Lessing (J.S.C.I., 1912, *31*, 465).

The conditions under which tests are carried out should be absolutely constant, and should approximate as far as possible to those mentioned above, but where facilities do not admit of the adoption of the standard method, a modified process will give results of great value to the individual experimenter, but these will not be comparable with the results obtained by other workers The usual temperature suggested is 950° C., but with modern coal-gas (420 to 450 B.T.U. per cubic foot), and using a Bunsen burner, the temperature of the coal in a platinum crucible is generally from 700° C. to 750° C. With a Meker burner, a temperature of about 900° C. can be obtained. A blow-pipe may be adopted, and one constructed on the principle illustrated in the " Engineer," 20th October, 1916, has been found to give a temperature up to 1,000° C., which can be maintained quite constant. Where possible, the temperature in the coal should be determined for a succession of tests under the standard conditions, by means of a pyrometer, preferably a thermo couple, but for a rough indication the melting point of potassium dichromate (940° C.) may be used. Under the most perfect conditions differences as high as 0·5 per cent. may be expected, but with separate individuals and conditions which are similar, differences may be found ranging up to 3 per cent.

The determination of volatile matter is of considerable importance, as valuable hints may be obtained as to the practical value of a coal, and of its behaviour during combustion or carbonisation.

The following are the main points: The value obtained during the test is called the " volatile matter " of the coal, which includes the moisture and the organic matter evolved during the ignition. When the percentage of moisture is deducted from the "volatile matter," the result is termed either the "volatile organic matter," or the "volatile combustible matter." The residue in the crucible represents the "coke," and the "fixed carbon" is obtained by deducting the percentage of ash from it.

Physical Appearance of Coke.

In carrying out the determination of the volatile matter, it is important to see that the coal is distributed evenly over the bottom of the crucible. At the completion of the test the appearance of the button of coke will then form a more valuable criterion of a particular type of coal. The button may vary in size, from one-half to 10 times the original volume of coal used. Whenever possible the button of coke should be preserved, and in the author's laboratory a special button is prepared and is fixed to a piece of stiff cardboard by seccotine, and after being labelled is filed for a certain period. Such buttons form a valuable means for the identification of changes in a seam, &c

The following is an outline of the terms used in describing different types of coke (Lunge, Technical Methods of Chemical Analysis, page 245)

Rough fine-grained	Black	Porous all over to near the edge.	1. Sandcoal (long flame dry coal)
		Fritted hard, porous in centre only.	2. Sintered sand-coal.
		Fritted hard all over	3. Sinter coal (long flame fat coal).
	Grey and hard, with blistered appearance.		4. Caking Sinter coal.
Smooth, lustrous, and hard.			5. Caking coal proper.

R. Lessing (J S.C.I., 1912, *31*, 465) describes a special apparatus for the determination of the volatile matter in coal at any desired temperature. The apparatus consists of a silica vessel which is heated electrically, and may be maintained at a constant temperature by means of an electrical resistance. The author has found that this apparatus may be maintained at any desired temperature for 12 hours at a time, without the need of adjustment. The system adopted at present for using the apparatus is to weigh one gram of coal into the silica tube, having allowed the temperature of the heating vessel to fall to 400° C. The silica tube containing the coal is then placed in the heating vessel, and the current turned on again. It has been found that the apparatus attains a temperature of 950° in two minutes. The coal is allowed to remain for seven minutes, when the tube is removed and placed in a desiccator to become cold, and is then re-weighed. The apparatus is at present being investigated in the author's laboratory, with a view to determining the best conditions under which the coal must be heated in order to simulate the results obtained by the ordinary crucible. It is possible to determine the agglutinating value, &c, in this apparatus with greater certainty than is possible with the crucible method.

The apparatus can be adapted for a number of purposes in the study of coals, and the one at present in use was partly constructed and assembled in the laboratory at an over-all cost of £7.

Calculation of the Calorific Value of Coal.

The calorific value of coal may be calculated with considerable accuracy from the results of the approximate analysis by applying a formula of the type of Goutal's. This will be dealt with in a separate bulletin—The calorific value of coal. (See also Bulletin 1, p 23).

The Agglutinating Power of Coal.

In dealing with caking coals, it is of importance to have a measure of the degree of agglutination of the coal, and the following tests may be carried out:—

Calais sand, or finely ground anthracite, or electrode carbon of a pre-determined size (*e.g.* passing through a 1/60's sieve, and caught by a 1/90's sieve) is mixed with the powdered coal in gradually increasing proportions. One gram of the mixture of ground coal and the inert material is then treated in the manner described for the determination of the volatile matter in coal. The button of coke formed is removed from the crucible, and its strength determined by placing upon it a 100 gram weight. When the button just powders under this pressure, the limit of the test has been reached, and the coal is said to have an agglutinating value equal to the smallest ratio of the weight of inert material giving such a button. For Lancashire caking coals the values vary from 1 of coal to 6 to 1 of coal to 26 of sand, *i.e.*, the agglutinating value varies from 6 to 26.

*Agglutination Curve.**

It has been found that the degree of fineness of the inert material is the chief factor to be considered in determining the agglutinating value of coal. If powdered electrode carbon is used and the agglutinating value determined for gradually decreasing size of particle, the values may be plotted. The curve formed is constant in form for the same coal, but fairly widely different for different seams. The curve has been termed the "agglutination curve."

The Increase in Volatile Matter due to the addition of Inert Matter.

Grounds and the author (Bulletin 3, Lancashire and Cheshire Coal Research Association) have found that a characteristic of coal may be established by determining the increase of the amount of volatile matter given off when gradually increasing amounts of inert matter of a standard size are mixed with coal.

According to the statements of Somermeier (Jour. Amer. Chem. Soc., 1906, *28-2*, 1002) the volatile matter is affected by the percentage of water present in the coal. This influence is stated to be comparatively small in the case of bituminous coals, but a difference of 25 per cent. may be expected when dealing with lignites He also states that the volatile matter is influenced by the degree of fineness of the coal, but the variation due to this fact is very small In his paper the following results are quoted :—

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* Grounds & Sinnatt.

	Moisture.	Volatile Matter. Per cent.
1/4-1/10	1·15	39·05
1/10-1/20	1·45	38 80
1/20-1/40	1·70	38·55
1/40-1/80	1·90	38·05
1/80 and finer	2·05	35 54

According to experiments carried out by Grounds and the author (loc. cit) upon Lancashire caking coals, little difference in volatile matter could be detected for widely different size of particles of the coal provided the whole of the sample was powdered to pass through the sieves.

The following table shows the results obtained upon certain samples of coal .—

Portion.	Degree of fineness of coal.	No. 1 Volatile organic matter. Per cent.	No. 2 Volatile organic matter. Per cent.	No. 3 Volatile organic matter. Per cent.
1	1/10-1/30	32·2	31·2	24·1
2	1/30-1/60	32·2	31·5	24 2
3	1/60-1/90	32·5	31·3	25·1
4	1/100-1/200	32 9	31·6	24·9
5	1/200 and finer	33·4	32·0	26·3

Experiments carried out in the author's laboratory upon the substitution of crucibles of different materials for platinum yielded the results given below; all the experiments were carried out under identical conditions.

	Approximate weight of crucible. Grams.	*Percentage of volatile matter.	
		No. 1 coal.	No. 2 coal
Platinum (standard)	29·5	32·4	34·2
Platinum	17·5	36·1	37·8
Nickel	23·7	32·3	34·8
Porcelain	14·6	33·2	36·1
Porcelain	21·7	31·0	32·2
Porcelain	25·0	29·1	32·0
Silica	14·4	31·7	33·7
Silica	23·2	28·4	31·9

It will be observed that a silica crucible weighing 14 grams yields values similar to those obtained by the use of a standard platinum crucible, and it has been found that if the silica crucible is fitted with a nickel or platinum lid, in place of silica, the results are improved.

Determination of Sulphur.

A considerable amount of experimental work has been done upon the determination of sulphur in coal, and the literature contains a description of a number of methods which may be considered accurate, but require either special conditions or re-agents. The majority of experimenters agree that Eschka's process is one of the most convenient for coals which contain not more than about 2 per cent. of sulphur, and the American Committee on Coal Analysis (J. Ind. Eng. Chem., 1917, *9*, 100) recommend the process for general use.

Eschka's method for the determination of Sulphur.

A fusion mixture, consisting of two parts of magnesium oxide (or calcium oxide), and one part of anhydrous sodium carbonate is required. The magnesium oxide should not be a compact heavy variety. Most authorities recommend the use of magnesium oxide, but no disadvantages will be experienced from the use of calcium oxide It has been found that pure calcium oxide is a more dependable re-agent than magnesium oxide When the fusion mixture has been prepared it is necessary to carry out a blank determination upon a pure organic compound free from sulphur, *e.g.* cane sugar or pure cellulose.

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* Tonge & Sinnatt (unpublished work).

Method. One gram of finely-powdered coal (through a sieve of 1/90 mesh) is intimately mixed with three grams of the special fusion mixture in a silica or platinum crucible. The mixture of coal and fusion mixture is now covered with a layer of fusion mixture to a depth of about one-eighth of an inch (about one gram) The crucible is heated gently over a small spirit lamp, or over a Bunsen burner. In the latter case, it is absolutely essential that the crucible should be protected from contact with the products of combustion of the gas. This preliminary gentle heating should be continued for about 10 to 15 minutes. The crucible is then placed in a muffle (electric, or one in which the products of combustion of the gas do not come into contact with the crucible), or in a circular perforation cut in a sheet of asbestos, held in an inclined position. By these two means, the products of combustion from the gas are removed from the neighbourhood of the crucible. Another method described by C. Bender (Zeit. Angew. Chem., 1915, Vol. 18, p 293) is to place the mixture of coal and Eschka's mixture in a hard glass tube, 18 c.m long, and 3 c.m. in diameter, which is closed at one end. The tube should be clamped in a horizontal position and heated in the ordinary way. It is desirable to stir the coal and fusion mixture during the ignition, but it is not absolutely essential. At the end of 1 to 1½ hours no traces of carbon will be found to remain, and the residue is a yellowish or greyish mass, depending upon the amount of iron present.

The contents of the crucible are transferred to a beaker, 50c. c.m. of water are added, a slight excess of bromine water (30c. c.m.) and the liquid is then gently heated. Dilute hydrochloric acid is added, until the liquid is distinctly acid in reaction. It is then evaporated to dryness and heated to about 110° C.

for about half an hour. The residue is then treated with water and hydrochloric acid, and the silica is removed by filtration. (An alternative method of treatment is to cool the mass, digest it with water (100c. c.m) and filter, and repeat the extraction with water. Thirty c. c.m of bromine water are added, and then hydrochloric acid, and the determination is then completed in the usual manner.) The liquid, or filtrate, is heated to boiling point, and treated with a small volume of ammonium chloride, and then a hot solution of barium chloride, and after being allowed to simmer for a short time and stand for one hour, the barium sulphate is separated by filtration. The precipitate is thoroughly washed with water, and the filtrate and washing water are carefully collected. The filter paper containing the barium sulphate precipitate is dried, ignited in the usual manner, and the weight of barium sulphate determined

Estimation of Iron.

The filtrate and washing water mentioned above are cooled, and the amount of iron present in it determined by titration, with a standard solution of titanous chloride, using potassium thiocyanate as the indicator (Knecht and Hibbert, Reduction Methods, p. 49 , Longmans, Green & Co.). The presence of barium, &c., does not interfere with the determination of iron.

The procedure given above has been found uniformly successful for routine purposes ; it is a rapid process for the estimation of iron. The latter is, of course, one of the important constituents in the ash of the coal, and a knowledge of the percentage present is usually a valuable indication of the chemical composition of the ash. These remarks apply especially if the same seam of coal is being examined frequently.

Method. A method for the rapid determination of sulphur is by the oxidation of the coal by means of sodium peroxide. A weighed amount of the coal is mixed with about 12 to 14 times its weight of sodium peroxide, placed in a special crucible, and ignited by suitable means (electrical , heating with a small Bunsen flame, or a small piece of hot nickel wire) ; these conditions are found in the Roland Wild calorimeter.* When the determination of the calorific value is complete in that instrument, the mass remaining in the nickel crucible contains the sulphur of the coal as sodium sulphate. It may be washed out and treated in the usual manner for the estimation of sulphuric acid. Parr (J Ind. Eng. Chem., 1919, *11*, 230; and Colliery Guardian, 1919, 1377) describes a special bomb for the above purpose, which is stated to yield accurate results. Precautions are required to prevent the reaction between the coal and sodium peroxide proceeding with explosive violence. As a rule, the peroxide method yields low results.

Method. Sulphur may also be determined by passing the gases present in the bomb calorimeter at the completion of a determination, into a dilute solution of caustic soda containing bromine. The contents of the bomb are afterwards washed out with distilled water, and the whole of the liquids collected together. The solution is heated to complete the oxidation, and the sulphuric acid is estimated gravimetrically in the usual manner. This method is rapid, but tends to yield low results (3 per cent or more too low).

Regester (J. Ind. and Eng. Chem., 1914, *6*, 812) has shown that 95 to 98 per cent. of the sulphur is converted into sulphur trioxide in the bomb, provided nitrogen is present in sufficient amount to form the oxides of nitrogen required to act as catalyst. It is advisable not to sweep the air out of the bomb before commencing a determination, unless the compressed oxygen contains at least 6 per cent. of nitrogen.

Determination of Nitrogen.

The determination of nitrogen in coal is more laborious to carry out than any of the tests described up to the present, and the knowledge gained is not of particular moment when the coal is being burned in ordinary grates. From the standpoint, however, of the conservation of the resources of the nation, it becomes increasingly important that the percentage of nitrogen present in every seam of coal in the country should not only be known, but the variations taking place during the working of the coal should be recorded. Under an efficient policy of fuel control, seams containing a high percentage of nitrogen should be conserved within the country. It should be made impossible for such coals to be consumed, except in processes in which the nitrogen is recovered in some form or other (*e.g.* coal-gas or coke manufacture, Mond gas manufacture or low temperature carbonisation for the production of smokeless fuels). It is interesting to recall that in pre-war times much of the coal exported from Great Britain to the continent contained a notably high percentage of nitrogen. In one particular year the average nitrogen content of the British coals purchased by one foreign nation was 1·9 per cent., which is far above the average percentage found in the ordinary coals worked in the country. As a rule, British coals contain about 1·5 per cent. of nitrogen, and these special coals were no doubt chosen by the foreign nation on account of the percentage of nitrogen present, combined with the other virtues generally associated with British coals. It is doubtful whether the merchants selling the coal were aware of the high percentage of nitrogen in the coal, and consequently of its enhanced value to the purchasers.

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*See special Bulletin on Calorific Power of Coal or Catalogue of Messrs. Alex. Wright and Co., Ltd., Westminster.

Determination.

Two methods for the determination of nitrogen are in common use, namely, Kjeldahl's and its modifications, and Dumas' process.

Kjeldahl-Gunning-Arnold Process.

From one to three grams of the dried coal, pulverised so as to pass through a 1/90 mesh sieve, or finer, are placed in a hard glass Kjeldahl flask (300 c.c.m. capacity) and treated with 30 c.c.m. of pure concentrated sulphuric acid. Ten grams of anhydrous potassium sulphate are added, and either 0·7 gram of metallic mercury, or one gram of anhydrous copper sulphate, the former being preferable. The flask is heated over a small naked Bunsen flame, until frothing ceases, and then continued until the liquid is quite colourless, and when this point has been reached, for a further two hours. The flame is then removed, and finely-powdered potassium permanganate is added. If the oxidation of the coal takes place sluggishly, potassium permanganate may be introduced as the digestion proceeds, but before each addition, the liquid must be allowed to cool. Kjeldahl recommends shaking in the potassium permanganate by means of a small sieve made from wide glass tubing, covered at one end with gauze having a fine mesh. The liquid in the flask is cooled, and diluted with about 300 c.c.m. of water and transferred to the centre flask (Fig. 2); caustic soda solution is added from the separating funnel until the liquid is alkaline, and 25 c.c.m. of a 4 per cent solution of sodium sulphide. The liquid is distilled, and the vapours passed into an excess of a normal solution of sulphuric acid. The excess of acid is subsequently determined by titration with a standard solution of ammonia, using cochineal as the indicator, or with caustic soda using rosolic acid or methyl orange as the indicator.

The apparatus shown (Fig 2) is considered to be the most satisfactory of all the forms described in the literature ; the liquid undergoes steam distillation, and the process therefore requires practically no supervision during the distillation, thus effecting a distinct economy of time in carrying out the determination.

A blank determination must be carried out to test all the re-agents used in the process, about one gram of a pure organic compound (cane sugar) being taken instead of coal.

Fieldner and Taylor (in Technical Paper 64, 1915, Bureau of Mines) give an exhaustive and conclusive study of the various methods of determining nitrogen. The chief conclusion they arrive at is that the presence of both potassium sulphate and mercury (or copper sulphate) are essential for the complete conversion of the nitrogen in coal into ammonia. They also show that the results obtained by Dumas' method are accurate, provided precautions are taken to remove nitrogen present in the copper oxide. They suggest that the copper oxide should be heated in a vacuum for several hours, and then cooled in an atmosphere of carbon dioxide.

Despite the above paper, it must be pointed out that Simmersbach and Sommer (Z. Angew. Chem., 1915, *28*, 481) cast serious doubts upon the accuracy of the Kjeldahl processes,

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and state that a modification of Dumas' method invented by them gives results which are up to 55 per cent. higher than those obtained by Kjeldahl's processes.

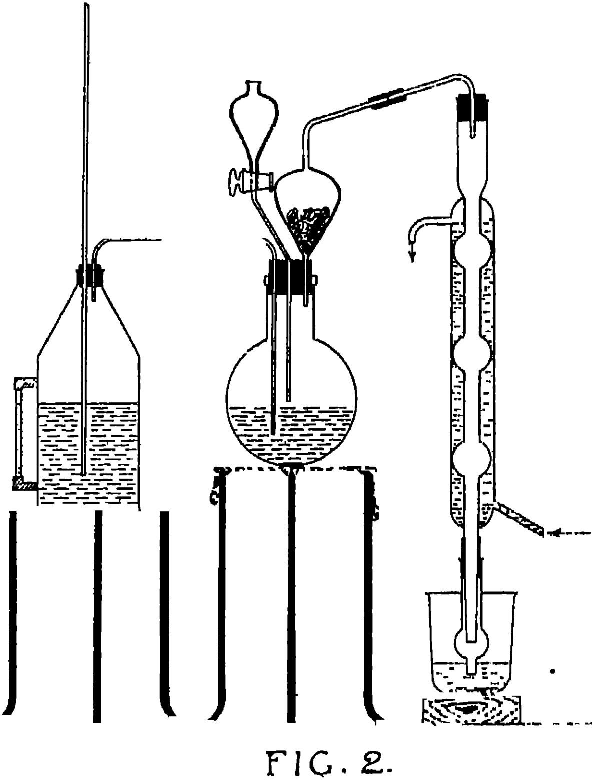

FIG. 2.

In a more recent paper Terres and others (J. Gasbeleuch, 1919, *52*, 173-192 ; J.S.C.I., 1919, *38*, 399t (good abstract)) describe results which show that all modifications of Kjeldahl's method yield low results owing to the evolution of nitrogen as such during the process. These experimenters have collected the nitrogen evolved during the process. They compared the results with the special Dumas' method, described by Simmersbach and Sommer, but modified it so that part of the oxidation of the compound could be brought about by oxygen. The following results show the order of the error of the Kjeldahl processes compared with that of the modified Dumas' method.

	Percentage of nitrogen.	
	Ruhr coal.	Anthracite.
Dumas' method and special final oxidation ..	1·55	1·72
Kjeldahl + potassium sulphate + mercury oxide	1·35 (7 hours)	1·31 (11 hours)
Kjeldahl + potassium sulphate + mercury oxide + copper oxide	1·36 (8 hours)	1·38 (10 hours)

Dumas' Method.

The method employed for ordinary organic compounds, which is described in text books on organic chemistry, can be used for the determination of nitrogen in coal. Certain precautions and novelties have recently been introduced into the process which will be found in the papers mentioned above.

Chlorine in Coal.

Comparatively little is known of the amount, and the method of occurrence of chlorine in coal. Certain Lancashire coals contain chlorine, the main proportion of which occurs in compounds soluble in water.

Two determinations should be carried out.

Total Chlorine. A weighed amount of coal is mixed with an excess of finely pulverised chlorine-free lime, and placed in a platinum crucible, which is inverted in a second large crucible, and the latter then practically filled with lime. The crucible is then heated, preferably in a muffle, until free from organic matter. The contents of the crucibles are washed into a beaker with water, and made slightly acid with nitric acid. The chlorine is determined in the liquid by Volhard's method.

In place of the above, Eschka's method may be used if quick lime is substituted for magnesium oxide in the fusion mixture.

Chlorine Soluble in Water. A weighed amount of the powdered coal is extracted with water under a reflux condenser, the coal is then separated by filtration, and the chlorine in the filtrate determined by Volhard's method.

According to J. W. Cobb (J. Gas Lighting, 1916, *133*, 684), even when coal is finely divided, extraction with water is imperfect. He advises grinding the coal to pass through 1/12 and be caught by 1/50 mesh sieve, and extraction first with water for four hours, and later with 10 per cent. nitric acid for about four days. He quotes the following, showing the composition of the soluble salts extracted by water from 100 grams :—

	Coal A.	Coal B
Na(K) ..	0·165	0·161
Mg ..	0·0034	0·013
Ca ..	0·014	0·0514
Cl ..	0·121	0·352
SO_4 ..	0·0064	0·0125
Total	0·3098	0·5899

Two other coals yielded 0·794 per cent. and 0·618 per cent. after extraction with water and nitric acid.

The following values are quoted by Wade (Analyst, 1916, p. 146) :—

	Per cent.	Per cent.	Per cent.
Total chlorine determined by ignition ..	0·253	0·015	0·344
Total chlorine extracted by water	0·251	0·019	0·346

He states that it would appear that the whole of the chlorine in coal is present as chlorides soluble in water.

Determination of Carbon and Hydrogen.

The accurate determination of carbon and hydrogen in coal presents greater difficulties than will be experienced with ordinary organic compounds.

Coal may contain a comparatively high percentage of sulphur, ash, and nitrogen, and a small amount of chlorine, for which special precautions are required in the combustion process.

When certain coals are heated a sudden and voluminous outburst of volatile compounds occur, which are mainly gaseous. The coke produced may be hard, and difficult to oxidise, and this factor is also influenced by the temperature at which the coke is formed.

No method exists for the absolute determination of the total moisture in coal, thus little is known of the water of constitution of the inorganic constituents in coal. This water is not evolved when the coal is heated to 105° C., but is driven off at the higher temperature prevailing during the combustion. On p. 14, it is shown that the ash present in particular samples of coal resembles kaolin in constitution: this should therefore contain about 13 per cent. of moisture in the natural state. Further, the shales associated with coal may contain about 13 per cent. of water of constitution. If the ash present in a sample of coal is 10 per cent., it would mean that the original inorganic compounds contained 1 per cent. of water of constitution, and consequently the hydrogen found in the combustion would be about 0·1 per cent. too high from this cause alone.

Many Lancashire coals contain carbonates, usually in the form of calcium carbonate, or substituted calcium carbonates, *e.g.* ankerite (calcium, ferrous, magnesium carbonate of varying composition). These compounds are decomposed during the combustion, and the carbon dioxide produced is determined with that formed by the oxidation of carbon. This tends to increase the percentage of carbon found in the coal (5·0 per cent. of calcium carbonate is equivalent to 0·6 per cent. of carbon). If the percentage of carbon dioxide the coal will evolve has been determined, a correction should be made in the carbon found during the combustion.

The Combustion Process.

The process will be found described in great detail in text-books on organic chemistry; for coal the principles are the same, but the tube should be packed in the following manner —

Commencing at the inlet end (Fig. 3) (to which is connected a supply of air and oxygen freed from moisture and carbon dioxide and under slight pressure), about 2in. in length of the tube are left empty and allowed to project outside the combustion furnace. There is then a short spiral of copper gauze or a diffusion bulb of refractory glass to prevent gases passing backwards along the tube or forming an explosive mixture. The next part of the tube contains the porcelain or silica boat, containing 0·2 gram of coal, pulverised to pass through a 1/90 mesh sieve; the coal may be either air-dried or dried coal and should be evenly distributed throughout the boat. The boat should have a free space of about 1in. at each end; the next 7in. of tube are filled with granulated or wire copper oxide, and this should be followed by 7in. packed with fused lead chromate. The lead chromate should be broken to pass through a sieve of 1/4 mesh and be freed from all material below a 1/10 mesh. Both the oxide and chromate are held in position by plugs of ignited asbestos. If the coal is very rich in chlorine a small amount of silvered pumice may be introduced after the lead chromate as an extra precaution. Following this is a freshly reduced spiral of copper gauze; there should remain about 4in. in length of tube, which is usually empty. The weighed calcium chloride tube (all glass as in figure) is connected directly to the combustion tube by a

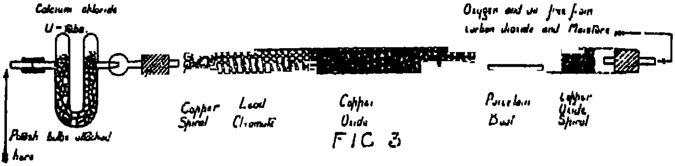

FIG 3

short, well-fitting rubber stopper, the potash bulbs are attached to the calcium chloride tube, and should be protected by a second calcium chloride tube.

The following is a brief description of the routine of the determination: If the tube or its contents are new or have stood some time, the whole, except the reduced copper gauze, should be heated and a current of air admitted for at least one hour in order to remove any moisture or carbon. All the burners, except those under the lead chromate, and half the copper oxide most distant from the boat are extinguished and the tube allowed to cool. The spiral of reduced copper gauze is then placed in the tube and the weighed calcium chloride tube and potash bulbs attached The boat containing the weighed amount of coal is introduced and the diffusion bulb or spiral replaced. Oxygen is turned on and the diffusion bulb heated first, and then the reduced copper spiral. The heating of the tube should now be made to converge upon the coal, the preliminary heating of which should be carefully controlled until the evolution of the volatile matter has occurred. The whole tube may be heated strongly and the speed of the combustion governed by the glowing of the coal. The stream of oxygen is replaced by air five minutes after the glow has ceased. After about two litres of air have passed through the tube, the calcium chloride tube and potash bulbs are removed and allowed to cool, in a position having level atmospheric conditions, and re-weighed at the expiration of 30 minutes. The boat is removed, carefully examined, allowed to cool in a desiccator and re-weighed. The ash should be inspected to determine whether any carbon remains and if any part of it has fused; if the latter has occurred, the masses must be broken and carbon again looked for.

The gain in weight of the calcium chloride tube is the water from the oxidation of the hydrogen, the free water, and the water of constitution.

The gain in weight of the potash bulbs is due to carbon dioxide, formed by the oxidation of carbon and by the decomposition of carbonates.

Oxygen in Coal.

As no direct method is known for the determination of oxygen in coal, the percentage can only be arrived at by difference. The value is therefore open to the accumulated errors of the whole of the analysis. Certain assumptions are required which are of very doubtful accuracy, with the result that the percentage of oxygen found may differ considerably from that actually present, unless the investigation of the coal is very exhaustive. The value is of considerable interest, as a classification of coals has been based upon their oxygen content, and the percentage is also required if it is desired to apply any formula for the calculation of the calorific value from the results of the chemical analysis. From a knowledge of the oxygen present in coal the percentage of hydrogen available for the production of gas (the disposable hydrogen) may be calculated, and a rough idea may be formed of the probable amount of aqueous distillates the coal will yield on being carbonised.

The following is a brief summary of some of the points it is necessary to consider in attempting to arrive at the percentage of oxygen in coal.

Ash. The percentage of inorganic compounds, as distinct from the residue left on ignition, must be deduced as accurately as possible. As pointed out under the analysis of ash, the actual partings occurring in the coal should be analysed. If the assumption is then made that the carbon dioxide found, when the coal is treated with acids, is present in this form, the actual amount of the compounds may be calculated. The excess of iron may be considered to be present as pyrites. The aluminium, calcium, alkalies, and silica will occur as natural silicates, the composition of which will determine roughly the number of molecules of water of constitution present. The hydrogen this water contains is deducted from the amount found by combustion, the result being the true amount of hydrogen in the coal.

Water. The water in coal occurs in at least two forms—that driven off at 105° C., and the water of constitution mentioned above.

Sulphur. The sulphur required to combine with the excess of iron mentioned above is calculated and deducted from the total; the difference may be assumed to be present as part of the organic substance of the coal. If any doubt exists about this point, the amount of sulphur occurring as sulphate should be determined.

Nitrogen. Nitrogen is generally considered to occur in the organic substance of the coal

Carbon. The true percentage of carbon is found as described under the combustion

The sum of. The inorganic compounds (plus the water of constitution of the clays); the water driven off at 105° C.; the organic sulphur; the nitrogen; the true hydrogen and carbon is deducted from 100, when the value is the percentage of oxygen in the coal.

Disposable Hydrogen.

For certain purposes it is convenient to assume that the hydrogen in the coal substance re-acts with the oxygen present as soon as the coal is heated; the water formed constitutes a portion of the aqueous distillate always associated with the carbonisation of coal. If, for example, a coal contains 4·5 per cent. of hydrogen and 8 0 per cent of oxygen, the disposable or available hydrogen is 3 5 per cent., *i.e.*, 4 5 per cent. less the amount of hydrogen which will combine with 8·0 per cent of oxygen (viz., 1·0 per cent.).

The following tests are not included under the chemical analysis of coal :—

The determination of the calorific value.

The examination of the character of the coal from the point of view of coal washing—including the determination of the specific gravity and the composition of the occluded gases.

The determination of the temperature of spontaneous ignition and glow.

The carbonisation on a small scale.

The microscopical examination.

The examination of the coal during its commercial application

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I wish to place on record my thanks to Miss P. Wray for her help during the preparation of this manuscript, and I am indebted to Mr. A. Grounds, B.Sc., A.I.C., for his kindness in preparing the drawings.

7151

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

COAL DUST *and* FUSAIN

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PRICE
ONE SHILLING

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PREFACE

The investigation contained in the present bulletin is obviously incomplete, but the members of the Research Association feel that in view of the interest attached to the results it is desirable to place them on record, especially as considerable time may be required for the completion of the work.

As mentioned in a previous preface (Bulletin No. 3), it is not the intention of the Association to allow work to accumulate, and to publish it in lengthy reports or papers, but rather to place reliable information before the industry as quickly as possible, in what we consider to be a convenient form.

We welcome any suggestions, especially from other coalfields, in order that the work we are undertaking may be given a wider interest than that associated with the coals from one field.

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President of the Lancashire and Cheshire
Coal Research Association.

Atherton Collieries,
Atherton.

COAL DUST *and* FUSAIN

Introduction.

During the examination of the characteristics of the chief seams in the Lancashire coalfield, it became necessary to investigate the Fusain (mother of coal, mineral charcoal, suddy parting, carbonised wood) associated with the various coals. The chief object of the work was to determine the composition of the fusain and the amount present in the dust produced during the working of the coal at the colliery The investigation is being continued with the special object of determining (1) the amount of fusain present in different coals, (2) the properties of the fusain with especial reference to the temperature at which it will ignite, (3) the influence of the fusain upon the general properties of the coal or coal dust in which it occurs.

Literature of Fusain.

The literature of the subject is fairly full on the paleobotanical side, and Tideswell and Wheeler in their recent paper (J.C.S., June, 1919), indicate the relationship which may exist between a particular specimen of fusain, and the coal in which it occurs.

J. J. Stevenson, in the Proceedings of the American Philosophical Society, 1911, 1-116, after describing the various ways in which fusain might be formed, states that it usually contains less volatile matter than the enclosing coal, and that the percentage of volatile matter varies between 6·4 and 30·7 per cent., but that in certain specimens a very high percentage of volatile matter was found, namely, 48·1 per cent. in coals underlying the Homewood sandstone A specimen containing 11·3 per cent. of volatile matter was associated with the coal containing 26·5 per cent, but, in another case, the average of a number of analyses showed that fusain could contain 20·9 per cent., and the surrounding coal only 17 per cent. In this paper it is suggested that the volatile matter of fusain bears a relationship in quantity to that of the enclosing coal

With reference to the percentage of volatile matter found by this experimenter, it will be shown that fusain frequently contains coal intimately mixed with it, and this may be the reason for the percentages of volatile matter found It may be remarked that no specimen of fusain obtained from Lancashire coals has been found to contain a greater percentage of volatile matter than the coal with which it is associated.

In Tideswell and Wheeler's paper, coal from the Hampstead colliery was investigated; fusain occurred containing 22 per cent. of volatile matter, whilst the surrounding coal varied between 38·6 and 40·8 per cent.; the ash present in the fusain is stated to be 10 per cent., and that in the surrounding coal to be from 1·2 to 3 6 per cent

The analysis given by Wheeler for fusain is as follows :—

Approximate Analysis.

	Per cent.
Moisture	3 9
Ash	10·0
Volatile matter per cent. on ash free dry coal	22·6

Ultimate Analysis.

Carbon	84·7
Hydrogen	3·9
Nitrogen	1·05
Sulphur	0·65
Oxygen	9·7

Stopes and Wheeler (Constitution of Coal, p. 23) state that it would seem "that the composition of the ash of fusain is fairly uniform, judging from the following analyses, Green et alia (1878)":—

	Ash of Fusain.	
	Better Bed. Per cent	Haigh Moor. Per cent.
Silica	38·7	36·1
Alumina	33·9	28·7
Ferric oxide	6·9	18·3
Lime	9·8	4·5
Magnesia	2·8	0·7
Sulphuric acid	7·7	7·6
Alkalies, &c.	0·3	4·1

The ash from a number of specimens of fusain obtained from Lancashire coals has been examined, and the following two are quoted to indicate that the composition of the ash of fusain may vary over wide limits.

Analysis of Ash of Fusain.

	Fusain Ash. (Ravine Mine) Per cent.	Fusain Ash. (Mountain Mine) Per cent.
Silica	8·37	37·78
Iron oxide	45·72	4·94
Aluminium oxide	9·21	33·06
Calcium oxide	12·64	9·81
Magnesium oxide	2·18	2·14
Sulphur trioxide	18·18	8·22
Alkalies and loss	3·70	4·05
Colour	Light brown.	Practically white.

Occurrence of Fusain.

Fusain occurs widely in Lancashire coals, but the amount present varies considerably. There appear to be at least two distinct forms of fusain; the first is a hard compact variety occurring rather rarely, which cannot be pulverised by pressure of the fingers; the second type is the common substance, and is dealt with in these notes. It appears to be present in Lancashire coals in two forms; as plates, bands, or in large lumps (one specimen found in the Peacock Mine weighed 3¾lbs.); and, secondly, as a powder distributed over the surface of the coal. In certain seams the fusain forms a network throughout the mass of coal, the planes not being more than ¼in apart. As fusain possesses little cohesive power, coal fractures most easily along the planes in which it occurs, and in view of this, the surfaces of coal are covered with a layer of fusain This of course does not apply when the whole of the coal is being pulverised, or a considerable grinding action is taking place, but mainly where it is being broken by fracture. The layers of fusain (which generally contain less moisture than the associated coal or lose moisture more rapidly) quickly change to a flocculent powder, when the surfaces on which they are deposited are exposed to the air, and the dust produced from the coal naturally tends to contain a higher proportion of this substance than of the coal itself. It will be shown later (p 14) that this phenomenon appears to have a distinct bearing upon the composition of the dust from coal, and especially upon that of the dust occurring in the mine, the screen rooms, &c.

Physical Properties of Fusain.

Fusain is a jet-black powder, which retains its black colour when pulverised to a fine state of division, *e.g.*, to pass through a sieve of 1/200 mesh, whereas bituminous coals, ground to a similar degree of fineness, frequently yield dust the colour of dark mahogany.

Fusain causes a black and dirty smudge on the skin, which has an appearance similar to that produced by charcoal. It is removed from the skin with difficulty, as it seems to have a greater affinity for the perspiration than coal dust, probably owing to its highly porous nature. An emulsifying agent (soap) is necessary to remove it, and it has been found that the skin is cleansed more thoroughly when fusain is present than when soap alone is used

Fusain has a needle-like structure, whilst particles of bituminous coals, of the same degree of fineness are, as a rule, more rounded. Fusain may therefore be distinguished from coal dust by means of the microscope. When a mixture of coal and fusain is sieved, the particles of fusain passing through a particular size of mesh tend to be larger than the particles of coal, owing to the comparatively greater length of the units of fusain compared with their breadth

Fusain ignites with considerable ease at a low temperature, and continues to smoulder at a dull red heat Many examples have been met with of this material continuing to smoulder without the production of flame, or the evolution of compounds having an odour, thus differing fundamentally from coal under similar circumstances The fact that little odour is produced adds to the dangers associated with the combustion of fusain, as practically no indication is afforded of the substance being on fire.

The following experiments indicate the manner in which fusain burns. A briquette measuring 4in. by 4in. by 9in. was made by mixing fusain with water , it was dried at a temperature of about 105° C. and allowed to stand for one week. The briquette was then placed on a stone slab, and the tip of one corner heated to redness by means of an ordinary match The briquette was allowed to remain undisturbed, and in about an hour the whole of it was consumed without the production of smoke or flame ; there was no evidence of combustion except a faint pleasant aromatic odour, resembling that of pitch-pine. The mass smoulders internally, for when the surface is removed, a glowing dull red zone is exposed. The residual substance, in certain experiments, was a finely powdered coke—in fact, it appeared as if the volatile matter only had been consumed ; in others the residual substance was the ash A briquette of similar dimensions, containing 50 per cent. of fusain and 50 per cent coal, acted in the same manner, and again practically no odour or smoke was produced.

This experiment was repeated in a number of ways; small heaps were made and the same method of ignition employed, with results which were similar to those described, but in many instances nothing remained except the ash of the material. Dusts from the following sources were examined · a dust collector, a screen room, the froth from a coal washer, all of which contained fusain, similar results being obtained. Fusain appears to play the part of a touchwood or tinder, assisting the combustion of the finely-powdered coal. One case may be cited of the dust from a dust collector becoming ignited by the heat from an electric globe which was placed near to it.

Reference may be made to an experiment carried out for Mr. J. B. Atkinson, H.M. Inspector of Mines, Newcastle-on-Tyne (Inst Mining Engineers, 1909, *39*, 742), on wind-borne dust, in which it was found that if the dust is placed in a cone, and heat applied to the top of it, the dust would eventually—if the experiment were successful—become red-hot throughout, and the heat would permeate the whole mass. (The combustion spread throughout the mass, and the plate on which it stood was cracked by the heat developed.) Mr. Atkinson stated that "whether that was due to the occluded oxygen or not he did not know—that was a matter for chemists."

Mr Atkinson also remarked that "Dr. Bedson's experiment had shown that the fine dust at the face or the fine dust from freshly-ground coal was more readily inflammable than the dust on the haulage roads, the latter dust being, notwithstanding, the more dangerous, because in the first place it was very fine; secondly, it was in situations where it readily formed a cloud (that was on the upper surfaces of the road); and, thirdly, it was accompanied by a swift current of air"

He further stated that "a good deal of coal dust came from the screens on the surface; it was brought down the shaft, and the coarser particles settled like the sands from a river, first, the finer particles or mud being carried farther in and settled on the timber." It is unfortunate that the chemical composition of the dust mentioned in the above experiment was not given. The action is similar to that recorded in our experiments.

Coke from Fusain.

When fusain is carbonised, no external evidence of the formation of coke is visible, as the latter has an appearance identical with that of the original substance. This might be expected, as the amount of volatile matter evolved is small, and is practically free from tarry matter.

The coke from fusain is quite deficient in caking power, and its volume is about the same as that of the original substance.

The coke is jet black in colour, and thus may be distinguished from ordinary coke, which is generally grey in colour. It follows that the presence of fusain in coal dust may have a considerable influence upon the caking index or the agglutinating power of the natural dust from coal, and also upon the agglutinating power of the slurry or fine material from coal washers; in fact, it acts as finely pulverised inert material. Grounds and one of us have shown that the degree of fineness of the inert material with which coal is mixed has the greatest influence upon the caking properties of the coal. (J S C I, 39, 83)

Method of Separating Fusain

The material was separated by breaking lumps of coal, and removing the fusain with a spatula when it was present in the form of sheets, or by brushing it lightly from the surface of the coal It was air-dried and powdered by pressing it gently between the fingers, and the resulting material sieved through a sieve of 1/30 mesh. The portion which passed through was again gently pressed between the fingers. It was again sieved, and the portion which passed through a 1/60 mesh was assumed to be fusain In order to ascertain the composition of a characteristic piece of fusain, a special specimen which measured 4in. by 2in. by ½in. thick, found in the Ravine Mine, was broken in the manner described above. It was then air-dried, an average sample taken from it, and sieved quantitatively with the following results :—

	Per cent.
Remaining on a 1/30 sieve ..	.. 25·4
Between 1/30 and 1/60 sieve ..	. 33·6
Between 1/60 and 1/90 sieve ..	.. 35·3
Passing through a 1/90 sieve ..	.. 5·7

The colour of the above fractions showed a distinct variation, the finer portions being a more intense black colour than the coarser portions.

Upon analysis the fractions gave :—

Percentage	Coal remaining on a 1/30 mesh sieve.	Fusain through 1/30 to 1/60 mesh sieve.	Fusain through 1/60 to 1/90 mesh sieve	Fusain through a 1/90 mesh sieve.
Moisture.. ..	1·50 ..	0·90 ..	0·55 ..	0·70
Ash .. .	17·50 .	10·00 ..	5·89 ..	6·70
Volatile matter .	24·20 ..	16·24 ..	11·97 ..	11·73
Vol. org. matter	22·70 .	15·34 ..	11·42 ..	11·03
Coke	75·80 ..	83·76 .	88·03 .	88·27
Fixed carbon ..	58·30 .	73·76 ..	82·14 ..	81·57
Sulphur .. .	5·96 ..	3·54 ..	2·34 ..	2·82
Colour of Ash ..	Maroon .	Maroon. .	Brown. .	Light maroon.
Nature of coke .	Dull grey, very hard, a compact flat button.	Dull grey, incoherent.	Dull grey, incoherent.	Dull grey, incoherent.
Iron in ash ..	31·6 ..	30·3 .	33·2 ..	35·0

It is evident that the portion remaining on the 1/30 sieve—25 per cent.—differed from the remainder of the material; in physical appearance it resembled an ordinary specimen of hard bright coal. No ordinary fusain could be detected in it by microscopic examination, and it could not be crushed by simple pressure of the fingers. It will be seen that its composition differs considerably from that of the coal (Ravine) with which the piece of fusain was associated (see p 14). It seems reasonable to suggest that coal associated with pieces of fusain may be somewhat different in composition from that of the coal of the seam itself

One reason for the examination of this piece of fusain was the notably high percentage of sulphur it contained, and it may be remarked that the coal-like portion contained a considerably higher percentage of sulphur than the fusain portion. The conclusion we wish to draw from the above values is that fusain may be pulverised with great ease, and that a high proportion of the resulting powder consists of material which will pass through a sieve of 1/60 mesh , further, material which will pass through such a sieve appears to be fusain in practically a pure form. This is shown clearly from the analyses, as the part between 1/60 and 1/90 mesh has practically the same composition as material which passes through a 1/90 sieve. The fusain from different sources appears to differ in the size of its particles.

The following tables have been prepared to show the composition of a number of samples of fusain, compared with the coal with which it is associated The fusain was collected by breaking lumps of coal, and brushing the material from the surfaces thus exposed; proximate analyses were carried out on the air-dried material, and ultimate analyses on the material dried at 105° C. for one hour

1. *Bacon Mine. Upper King Coal.*

Percentage	Fusain.	Coal.
Moisture	1·23	2·16
Ash	10·86	3·72
Volatile matter	19 90	40·19
Volatile organic matter	18·67	38·03
Coke	80 10	59·81
Fixed carbon	69·24	66·09
Calorific value B.Th.U. per lb.	13,423	14,050

	Fusain.	Coal.
Carbon	77·30	76·96
Hydrogen	3·82	5·01
Nitrogen	0·79	1·62
Sulphur	1·62	1·98
Ash	11·00	3·80
Oxygen (by difference)	5·47	10·63
Carbon on moisture ash-free basis	86·7	80·0

The coal was very bright and glossy, and contained some partings of ankerite. The fusain was bright, bulky, and jet black in colour.

2. *Mountain Mine.*

Percentage.	Fusain.	Coal.
Moisture	0·45	2·73
Ash	7·14	3·52
Volatile matter	9·52	26·46
Volatile organic matter	8·87	23·73
Coke	90·68	73·54
Fixed carbon	83·54	70·62
Calorific value B Th.U. per lb.	13,968	15,040
Carbon	—	81·94
Hydrogen	—	5·28
Nitrogen	—	1·16
Sulphur	—	1·61
Ash	—	3·62
Oxygen (by difference)	—	6·39
Carbon on moisture ash-free basis	—	85·0

The coal was exceedingly fragile, and some pyrites partings were present. The coke from the coal was very bulky, porous and fragile.

3. *Hell Hole Mine—Newtown.—East end of field.*

Percentage.	Fusain.	Coal.
Moisture	0·70	1·94
Ash	6·71	2·67
Volatile matter	15·97	35·00
Volatile organic matter	15·27	33·06
Coke	84·03	65·00
Fixed carbon	77·32	62·33
Calorific value B.Th.U. per lb.	14,015	14,589
Carbon	83·26	82·25
Hydrogen	3·27	5·34
Nitrogen	0·84	1·62
Sulphur	3·36	1·02
Ash	6·76	2·73
Oxygen (by difference)	2·51	7·05
Carbon on moisture ash-free basis	89·3	84·5

The coal was black, shiny, and hard, and contained a fair quantity of fusain. No ankeritic partings were present.

4. *Arley Mine.*

Percentage.	Fusain.	Coal.
Moisture	1·40	1·92
Ash	4·72	3·23
Volatile matter	13·21	35·34
Volatile organic matter	11·81	33·42
Coke	86·79	64·66
Fixed carbon	82·07	61·43
Calorific value B.Th.U. per lb.	14,700	14,740
Carbon	84·63	82·32
Hydrogen	3·24	5·51
Nitrogen	0·76	1·54
Sulphur	2·11	1·45
Ash	4·79	3·29
Oxygen (by difference)	4·47	5·89
Carbon on moisture ash-free basis	88·9	85·1

Clean, black, strong coal

5. *Ravine Mine.*

Percentage.	Fusain.	Coal.
Moisture	1·50	2·42
Ash	11·22	4·05
Volatile matter	15·80	36·56
Volatile organic matter	14·30	34·14
Coke	84·20	63·44
Fixed carbon	72·98	59·39
Calorific value B Th.U. per lb.	12,880	14,360
Carbon	76·85	78·42
Hydrogen	3·47	5·24
Nitrogen	0·73	1·50
Sulphur	2·85	2·28
Ash	11·41	4·15
Oxygen (by difference)	4·69	8·41
Carbon on moisture ash-free basis	86·8	81·8

Fairly strong black coal with ankerite partings and some thin pyritic bands Gives a dense coke on coking.

The Composition of the Dusts from Mines.

As we have been unable to find any reference to the percentage of fusain in mine dusts, it appeared to be of interest to determine the amount present. A number of samples of dust were obtained from two separate pits from the Arley Mine, the first sample being collected from the floor of the pit, within about 10 yards from the working face. Every care was taken to obtain a representative sample of dust, and for the purposes of this test a place which had not been stone-dusted was chosen. It has been found that the volatile organic matter in artificial mixtures of fusain and coal varies with the proportion of the constituent present within the limits of experimental error.

The percentages of fusain present in the dusts were calculated from the following:—

Fusain Volatile organic matter on ash and moisture free basis = 12·0 per cent.

Coal: Volatile organic matter on ash and moisture free basis = 35·0 per cent.

It has been found that the volatile organic matter of mixtures of fusain and coal agree with that obtained by calculating the values upon the percentage of each constituent, assuming its volatile organic matter to be as stated. Where it is proposed to carry out similar work, it is necessary to analyse the pure fusain and pure coal of any particular seam, when it becomes possible to carry out the above calculation.

Analysis of Samples of Mine Dust.

First Pit.—Arley Mine.

Percentage.	First sample.	Second sample.
Moisture	1·0	1·2
Ash	20·4	24·4
Volatile matter	21·7	21·4
Volatile organic matter	20·7	20·2
Coke	78·3	78·6
Fixed carbon	57·9	54·2
Fusain present	38%	34%

Second Pit.—Arley Mine.

Percentage.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No 4.
Moisture	1·3	0·9	1·4	1·4
Ash	28·7	10·1	23·2	19·2
Volatile matter	21·8	22·5	25·0	25·4
Volatile organic matter	20·5	21·6	23·6	24·0
Coke	78·2	77·5	75·0	74·6
Fixed carbon	49·5	67·4	51·8	55·4
Fusain present	25%	47%	16%	21%

In the case of the samples from the second pit, a special board was placed on the floor near to the working face, and the dust which accumulated upon it used for the analysis. It will be observed that all the samples of dust contained a low percentage of volatile organic matter, and when this value was calculated upon an ash and water free basis, it was still considerably below the amount present in the coal The reason for this lies in the fact that the dust contains a proportion of fusain, which reduces the volatile matter of the dust The amount of fusain present has been calculated upon the assumption that it contained 12 per cent. of volatile organic matter. These values were obtained under the conditions of the test for volatile matter which we adopted throughout the whole of this work.

Examination of the Dust from the Dust Collector attached to a Belt-picking Room.

This dust is formed during the process of hand-picking, or at a time when the coal is being broken by simple fracture. It is separated from the air by means of a dust collector. The dust was sieved quantitatively, and an average sample then analysed. The two main fractions from the sieving test were also analysed.

Approximate Analysis.

	Per cent.
Moisture	1·2
Ash	9·1
Volatile matter	22·6
Volatile organic matter	21·4
Coke	77·4
Fixed carbon	68·3
Fusain	49%

Quantitative Sieving Test.

	Per cent.
Above 1/30 mesh sieve..	0
1/30 to 1/60 mesh sieve	1·5
1/60 to 1/90 mesh sieve . ..	3 0
Through 1/90 mesh sieve .. .	95·5

Analysis.

Mesh of sieve. 1/30 to 1/90.	Per cent.	Mesh of sieve. Through 1/90.	Per cent.
Moisture..	2·1	Moisture	1·2
Ash	7·0	Ash	9·6
Volatile matter.. ..	31·3	Volatile matter ..	21·4
Volatile organic matter	29·2	Volatile organic matter	20·2
Coke	68·7	Coke	78·6
Fixed carbon	61·7	Fixed carbon	69·0
Fusain	13%	Fusain	54%

The material being dealt with at the time the sample was collected was Arley coal. It will be observed that the dust is in an extremely fine state of division, and contained approximately 50 per cent. of fusain. The colliery proprietors recognise that this dust is liable to take fire and to smoulder.

Examination of the Accumulation in the Slurry Separators of a Washery.

In one particular slurry tank, the fine dust from the washery and the dust from a dust collector are collected together as slurry, and the material is allowed to settle throughout a period of one week; during this period about 100 tons of slurry accumulates. A typical tank containing 100 tons of it was taken, and a section carefully cut from top to bottom, each successive 6in. in depth being collected in a separate vessel. The analyses of the material in the slurry tank are given in the following table.

In the last column the proportion of fusain present is given, calculated by the method mentioned earlier in this paper:—

No. 1 Washery (Slurry or Dant Tank).

Slurry.	Moisture.	Ash.	Volatile organic matter.	Percentage of fusain.
0in.— 6in.	1·90	6·0	21·3	52
6in.—12in.	2·0	10·9	26·1	22
12in.—18in.	7·7	10·6	24·0	24
18in.—24in.	6·8	10·6	25·4	19
24in.—30in.	3·4	9·6	27·5	15
30in.—36in.	5·3	11·2	26·4	15
36in —42in.	7·1	13·4	24·0	21
42in.—48in.	8·3	13·3	21·9	31

The above analyses show conclusively that most of the material collected in the slurry tank contains a relatively high percentage of fusain. It is well known that such material is difficult to dry, and this may be due to the presence of the fusain. When it is realised that fusain yields a non-coherent coke, it will be seen that this fine material has a deleterious effect upon the coke produced. It has been shown by Grounds and one of us that very finely divided inert material possesses the property of reducing the caking power of coal, and it follows that as fusain possesses no caking power, the coke produced from coal containing any quantity will be less coherent than that obtained from pure coal. It may be pointed out that the top 6in. of material collected in the above slurry tank yielded coke which was absolutely deficient in caking power, although the coal with which it was associated has an agglutinating value equal to 14 parts of sand. Every section of the above tank yielded coke which was less coherent than the pure coal. It is the practice, where the coal is being used for coke making, to mix the fine slurry with the coal previous to carbonisation. Our tests indicate that the effect of the fine material is probably much more pronounced than is usually recognised, and that precautions should be taken to ensure efficient distribution of the fine material throughout the whole mass of the coal. If distinct layers of slurry are allowed to form, the coke produced will possess distinct lines of weakness, and consequently be more fragile

It is not proposed to discuss in detail the results given in this bulletin at the present stage of the work. It is clear that dust in mines and in places where the coal is broken by fracture may contain a considerable percentage of fusain.

Fusain is a flocculent and porous powder, and occurs in a fine state of division; this facilitates its suspension in a current of air.

Dust from a dust collector, of which 95 per cent. by weight would pass through a sieve of 1/90 mesh, was found to contain about 49 per cent. fusain.

From the experiments it is clear that in studying the properties of coal dusts a sharp distinction must be drawn between dusts produced by the natural fracture of the coal, and those formed by ordinary pulverisation. Results obtained upon the latter are valueless as an indication of the properties of the actual dusts found in the pit, screen room, &c., as these contain varying percentages of fusain.

It would appear that when a fire has been started in fusain, or in mixtures of fusain and coal dust, that the zone of combustion rapidly traverses the mass, and consequently the presence of fusain in the dust in the goaf and in mines generally, may have a marked influence upon the tendency any particular seam has to produce gob fires, and for the zone of combustion to spread

We wish to place on record our thanks to Miss P. Wray for her help during the preparation of this bulletin.

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

HOO CANNEL

INVESTIGATIONS OF THE STRATA ASSOCIATED WITH COAL—I.

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AND
M. BARASH, M. Sc. (Tech.)

PRICE
ONE SHILLING

BULLETIN 6
1920

PREFACE

The results of few investigations upon the strata associated with Lancashire coals have been published, and as the subject is one of general interest it appears desirable for the Research Association to examine such problems and place the details on record.

When this information has been at the disposal of the industrial world it is possible that applications may be found for the materials, and thus a greater use be made of the nation's mineral wealth.

R. A BURROWS,

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Coal Research Association

Atherton Collieries,
Atherton.

HOO CANNEL

Introduction.

Few publications appear in the literature dealing with the subject of low-grade cannel coals; it is therefore desirable to place on record the present study of the properties of a typical seam, with a view to the possible utilisation of similar deposits.

From the point of view of the conservation of the national resources, it is unfortunate that methods of utilising low-grade cannels on a large scale have not been more widely developed. It is obvious that suitable applications for such material are not easy to suggest, but it is thought that if the general characteristics of such cannels were more widely known, certain industries might find it economical to substitute the cannels for coal, either wholly or in part.

The term Hoo Cannel is largely used in Lancashire for cannels containing a high percentage of ash to distinguish them from low-grade shales, seams varying in thickness from a few inches to several feet occur in the Lancashire coalfield. The cannel is generally associated with seams of coal, and frequently forms the upper stratum. It possesses highly tenacious properties, and the coal parts from it with a perfectly clean fracture; for these reasons it forms an excellent roof for working the actual coal seams, and consequently it is a distinct advantage in many cases to leave the cannels in the goaf. The cannel shows practically no tendency to take fire in the goaf.

Hoo Cannel may be of interest in the following branches of industry :—

1. *Coal Gas Manufacture and Low-temperature Carbonisation.*

In view of the fact that the manufacture of coal gas is tending towards the complete conversion of coal into volatile products of carbonisation without the production of coke, Hoo cannel might find uses for this purpose. The disadvantage attending the high percentage of ash might be compensated for by the material being purchased upon the basis of its calorific value, and under such circumstances there appears little objection to the material as one from which highly efficient gas could be obtained ; the complete conversion of the carbon into water gas would be readily accomplished. Furthermore, it is suggested that the ash or clinker should form a marketable product.

2. *Pulverised Fuel and Cement Manufacture.*

The inorganic constituents of Hoo cannel are practically homogeneous in composition, and as the cannel is found to pulverise with ease (see p. 9), it appears to be a material which would find a distinctly economical application in the production of cement and as pulverised fuel. Pulverised Hoo cannel has been found to burn readily in an experimental burner.

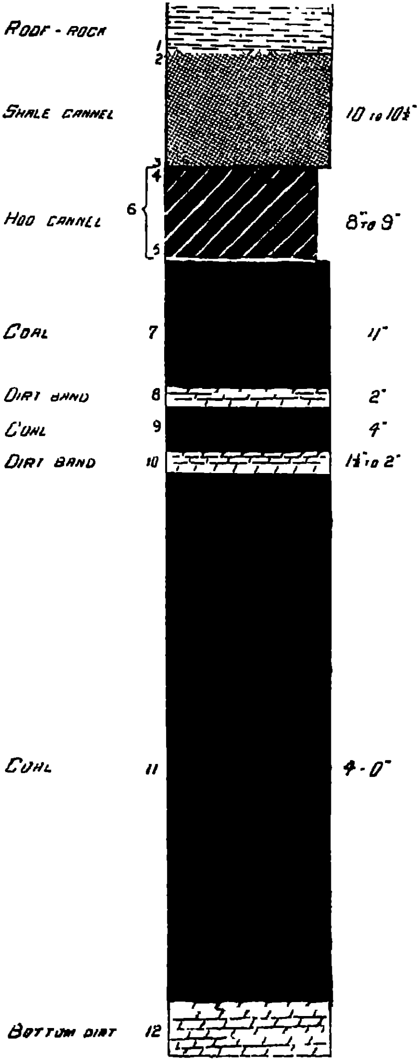
3. *Producer-gas Manufacture*

The percentage of nitrogen present in Hoo cannel, calculated on a basis of pure organic material, is quite as high as that in good bituminous coals In general properties Hoo cannel is entirely non-caking, and retains its form when undergoing carbonisation or oxidation. It therefore appears to be a material which should find a ready application in power producers, especially in those in which the removal of the ashes is facilitated by movable grates or ash pans.

The residue from (1) coke and (3) clinker, might form a filling material for light concrete, as it combines lightness with strength, durability and non-inflammability.

Examination of a Typical Seam.

The particular specimen of Hoo cannel examined in this bulletin was obtained from the district of Hindley, Lancashire. The section of the whole seam is shown in the diagram.


ROOF - ROCK
1
2
SHALE CANNEL
10 to 10½"
3
4
6
HOO CANNEL
8" to 9"
5
COAL
7
11"
DIRT BAND
8
2"
COAL
9
4"
DIRT BAND
10
1½" to 2"
COAL
11
4'-0"
BOTTOM DIRT
12

It will be observed that associated with the Hoo cannel, and lying above it, is a band of low-grade shale, and that the latter contains a considerable amount of organic matter; some portions are distinctly rich in volatile organic matter, whilst in others the amount of ash shows it to be an ordinary type of shale.

Chemical Analysis.

The accompanying table shows the proximate analysis of the strata associated with the band of Hoo cannel, and includes analyses of the shale and Hoo cannel at the top and the bottom of each layer, *i.e*, the top inch and the bottom inch of each band of material:—

Sample.	Description	Moisture.	Total Volatile Matter	Volatile Organic Matter.	Coke	Fixed Carbon	Ash
1	Roof Rock	0·41	35·92	35·51	64·08	—	68·86
2	Top Shale (top inch)	1 30	29·92	28·62	70·03	31·78	37·00
3	Top Shale (bottom inch)	1·72	19·74	18·02	80·26	17·14	61·40
4	Top Hoo Cannel	1·56	34·81	33·25	65·19	38·33	25·30
5	Bottom Hoo Cannel	2 15	33·15	31·00	68 85	40·88	23·82
6	Average Hoo Cannel	*2·10*	*33·70*	*31·60*	*66·30*	*39·78*	*24·42*
7	Top Coal	2·35	34·57	32·22	65·43	46·29	16·79
8	Dirt Band	2·30	15·95	13·65	84·05	7·84	73·91
9	Coal	2 02	37·50	35·48	62·50	48 79	11·69
10	Dirt Band	2·25	18·00	15·75	82·00	11·42	68·33
11	Main Coal	2·21	37·93	35·72	62·07	52·41	7·45
12	Dirt	2 23	16·55	14·32	83·45	7·22	74·00

Complete Analyses of Hoo Cannel (No. 6) and Coal (No. 11).

Determination.		Hoo cannel. Percentage.	Coal. Percentage.
Moisture		2·10	2·21
Volatile Matter		33·70	37·93
Fixed Carbon		39·78	52·41
Ash		24·42	7·45
Carbon		60·74	73·96
Hydrogen		4·23	4·19
Nitrogen		1·30	1·82
Sulphur		1·23	4·83
Oxygen (by difference)		8·08	7·75
Calorific Value	B.T.U.	11,000	13,890
	cals.	6,110	7,710
Calorific Value B.T.U. (ash free)		14,700	15,700
Pyridine extract, per cent.		9·5	27·1
S.G. (water=1000)		1,488	1,322
Weight in lbs./c ft		950	822

The Hoo cannel separates from the shale cannel with a clean parting, and the two bands of material are entirely distinct.

From the analyses it will be observed that the composition of the top inch of the band of Hoo cannel differs only slightly from that of the bottom, whilst the bottom of the shale cannel is of a distinctly inferior nature compared with that at the top. Some emphasis should be placed on this fact, as it appears to have been overlooked; bands of shale-like material being assumed to be homogeneous in character.

The upper inch of the top shale is comparable with a good type of Hoo cannel, whilst the lower portion is practically useless.

Observations on the Chemical Analyses.

Nitrogen. The percentage of nitrogen in the sample of Hoo cannel, calculated on an ash free basis, is comparable with that in ordinary bituminous coals, and on this account the products of carbonisation should contain a considerable amount of ammonia.

In the tests described later, no facilities were available for the complete recovery of the ammonia.

Sulphur. The sulphur content is rarely excessively high, and the highest encountered is 2·4 per cent.; generally about 1·2 per cent. is found. There is a marked absence of pyrites in Hoo cannels.

Volatile Matter. It will be observed that the volatile matter, calculated on an ash and moisture-free basis, is considerably higher than that found in bituminous coals, and from the point of view of the products of carbonisation the yield is considerably greater than that obtained from bituminous coals.

Coke. Every sample examined up to the present has yielded a non-caking coke, as a rule the coke retains the exact size and shape of the original piece of Hoo cannel, but is pierced by fissures. When the coke is burned the ash retains the form of the original piece of material.

Extraction with Pyridine.

It was found on extraction of Hoo cannel with pure pyridine, that an extract of only 12·7 per cent. (ash-free basis) was obtained, whilst the coal with which the Hoo cannel was associated, under parallel conditions yielded an extract of 29·4 per cent. It is therefore obvious that the organic substance of Hoo cannel differs in nature from that of ordinary coals.

Washing Tests.

Attempts were made to determine whether Hoo cannel could be improved by washing, and samples were pulverised to varying degrees of fineness and treated with calcium chloride solution of 1·35 specific gravity. No separation of the material into lighter and heavier portions was observed, and the conclusion must be drawn that the ash is an inherent constituent of the cannel substance, and no improvement can be effected by washing the material.

The Relative Ease with which Hoo cannel can be Pulverised.

A sample of Hoo cannel and of bituminous coal (Arley Mine) were broken up so as to pass through a ¼in. sieve, and be caught by a 1/10 sieve. One hundred grams of the sieved material were then placed in a small ball mill, and pulverised under exactly similar conditions of speed of rotation of the mill, &c. The samples were removed at intervals, and tested for the percentage which would pass through a sieve of 1/200 mesh.

The results are given in the following table :—*

	Time of grinding. Hours.	Percentage through a 1/200 mesh sieve.
Arley Coal	17	13·8
	22	40·0
	30	70·0
	34	93·0
Hoo cannel	2	43·3
	4	61·0
	6·5	80·0

The results indicate that Hoo cannel may be pulverised to pass through a 1/200 mesh sieve considerably more rapidly than a bituminous coal of the nature of the Arley Mine. On this account, it would appear that Hoo cannel would be an economical material for use in a pulverised form.

Analysis of Hoo cannel from Burnley District.†

Percentage.	No. 1	No. 2	No. 3	No. 4
Moisture	1·2	1·1	1·1	1·1
Ash	42·6	47·6	44·6	47·4
Volatile Matter	20·8	19·7	20·6	19·5
Volatile Organic Matter	19·6	18·6	19·4	18·4
Coke	79·2	80·2	79·3	80·4
Fixed Carbon	36·3	32·6	34·6	33·0

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* Burrows, Moore & Sinnatt (unpublished work).

† Bayley, Grounds & Sinnatt (unpublished work).

*Analysis of Hoo cannel from Bickershaw District.**

	Percentage.
Moisture	0·7
Ash	32·4
Volatile Matter	29·0
Volatile Organic Matter	28·3
Coke	71·0
Fixed Carbon	38·5

*Analysis of Hoo cannel from Garswood District, Wigan.**

Percentage.	No. 1	No. 2	No. 3	No. 4
Moisture	1·8	2·0	3·0	2·8
Ash	10·1	40·0	44·2	41·3
Volatile Matter	49·9	30·7	24·9	37·0
Volatile Organic Matter	48·1	28·7	21·9	34·2
Coke	50·1	69·3	75·1	63·0
Fixed Carbon	40·0	29·3	30·9	21·7

The Carbonisation of Hoo cannel.

In view of the fact that the investigation of a sample of cannel similar in nature to that at present under examination is described by T. F. Winmill, B.A., B.Sc. (Gas World, September, 1917), and a specimen of low grade shale by S. R. Illingworth, B.Sc., F.I.C. (J.S.C.I., 1919, *38*, 355T.), under conditions which were typical of low temperature carbonisation, it appeared desirable to examine the material from the point of view of ordinary coal carbonisation in the gas works.

An average sample of about 4 tons of the material (page 4) was obtained, and tests were carried out upon two separate tons of material at temperatures of 750° C. and 920° C. The lower temperature was selected as being typical of the minimum permissible for coal carbonisation in a coal gas works, and the higher as being roughly the temperature used in ordinary practice. The experiments were carried out in a complete experimental coal gas installation, which included a battery of four horizontal retorts each of 1 cwt. capacity, and the necessary subsidiary plant.

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* Bayley, Grounds & Sinnatt (unpublished work).

An average sample of the four tons of Hoo cannel was found to have the following composition :—

	Percentage.
Moisture	1·99
Ash	26·79
Volatile Matter	33·12
Fixed Carbon	38·10

On ash-free dry basis —

Carbon	82·98
Hydrogen	5·78
Nitrogen	1·73
Sulphur	1·70
Oxygen	7·81

The following are the results of the two tests :—

	A.	B.
	920° C.	750° C.
Total *Gas* made per ton	9,870 c. ft.	7,920 c. ft.
Corrected to N T.P.	9,820 c. ft.	7,770 c. ft.
Corrected to 16 c.p. gas	9,210 c. ft.	7,920 c. ft.
Candle power (c.p)	15·0	16·3
Calorific value of gas (B.T.U.)	521	562
H_2S in crude gas gr. /100 c. ft.	370	480
Coke, per ton	1,540lbs.	1,620lbs.
	68·9%	72·4%
Tar, per ton	8·0 gals.	11·5 gals.
	4·1% by wt	5·8% by wt.

Examination of the Products obtained from the Carbonisation.

Coke. The coke produced at both temperatures was similar in appearance, being almost black in colour ; it was compact in form but light in weight, and when fractured split into layers resembling slate. It was difficult to pulverise, and possessed none of the spongy texture usually associated with ordinary gas coke. It was found to burn readily in a producer, and in an ordinary fire grate.

The following are the analyses of the samples of coke obtained from the carbonisation tests —

Percentage	A. 920° C.	B. 750° C.
Moisture	3·02	3·11
Ash	39·50	34·58
Volatile Matter	5·50	5·86
Fixed Carbon	51·98	56·45
Nitrogen in coke calculated on air-dried sample	0·785	0·997
Nitrogen left in coke of original nitrogen in cannel	49·9	62·1

The Tar.

The samples of tar were found to separate readily from water, and after being well dried were fractionally distilled with the following results :—

Tar A obtained at 920° C. Density (D) =1·149 at 20° C.

Fraction No.	Temperature (°C.)	Per cent. by wt. yield.	Description.
1	up to 170	6·8	1st drop at 65° C. Pale yellow oil. D=0·885 and one-fifth of its volume aqueous.
2	170–230	15·5	Reddish-yellow oil. D =1·009 and completely solid at 9° C.
3	230–270	8·95	Greenish-yellow oil. D =1·039 and solidifies at about 5° C.
4	270–330	22·9	Mixture of red oil and yellow crystals. Mixture D=1·118.
	Residue.	45·0	Shiny, black, brittle pitch.

Tar B. obtained at 750° C. Density (D) = 1·136 at 20° C.

Fraction No.	Temperature (°C.)	Per cent. by wt. yield	Description.
1	up to 170	4·9	1st drop at 62° C. Pale yellow oil, D = 0·889 and one-fifth of its volume aqueous.
2	170–230	17·3	Appearance similar to fractions in A.
3	230–270	7·9	
4	270–330	28·2	
	Residue.	41·4	

These fractions were examined separately, and proved to be broadly similar to those obtained from ordinary coal tar. In other words, the products belonged to the benzene series, and not to the aliphatic (methane, &c) series.

This point must be emphasized, as there appears to be a general opinion that the distillation of Hoo cannel would lead to the production of tar which would contain a considerable percentage of the paraffin or methane series of hydrocarbons. These products are, of course, constituents of ordinary petroleum, and would be valuable as motor fuel. From the results of the present investigation it is proved that such statements are not correct for carbonisations carried out between 700° and 900° C, but that Hoo cannel yields products resembling those obtained from coal.

The fractions obtained from the distillation of the tar produced at 920° C. gave the following results :—

Fraction 1 was separated from the lower aqueous layer, washed with water, and then extracted with three washings, each of moderately strong H_2SO_4 and NaOH respectively. The washings yielded a very small quantity of phenolic and amino compounds. The residual oil was washed with water, dried over calcium chloride and re-distilled, giving a naphtha containing about 10 per cent. of its weight of benzene and boiling in equal increments from 60°–160° C. This mixture, on nitration, gave nitro-compounds completely soluble in cold concentrated sulphuric acid, indicating that it consisted solely of aromatic hydrocarbons, and contained no members of the fatty series of hydrocarbons. Yield = 13 gallons per ton of tar or ½ gallon per ton of cannel.

Fraction 2 washed in a similar manner gave :—

(*a*) 0·25lbs. of liquid amino-compounds per ton of cannel, *i.e.* 6·25lbs. per ton of tar.

(*b*) 5·5lbs. of phenolic bodies per ton of cannel, *i.e.* 137·5lbs. per ton of tar. Consisted of a mixture of phenol and cresols boiling at 185°–200° C. The residue was a semi-solid oil which yielded :—

3lbs. per ton of cannel or about 75lbs per ton of tar, of crude, dry naphthalene, m p. 78° C.

The residual oil, after filtering off the naphthalene, was again found to consist of aromatic compounds of a peculiarly pleasant odour.

Fraction 3 was treated in a similar manner and gave :—

(*a*) ¼lb of liquid amino-compounds per ton of cannel, *i.e.* 6¼lbs. per ton of tar.

(*b*) 1lb. of phenolic bodies per ton of cannel or 25lbs. per ton of tar, b p. 233°–240° C. Solidified on cooling. The residual oil again gave a further quantity of crude naphthalene and high-boiling aromatic hydrocarbons, the yield of the former being :—

2½lbs. per ton of cannel, or
62·5lbs. per ton of tar

The mixture of hydrocarbons again had a peculiar and not unpleasant odour.

Fraction 4, the largest, on standing separated into solid and liquid portions. The solid was filtered off, pressed between filter papers and yielded :—

3½lbs. per ton of cannel, or
87½lbs. per ton of tar of crude anthracene. A much larger quantity of this was obtained from the filtered oil after washing as above, and then allowing to stand overnight.

Total yield of crude anthracene —

15lbs. per ton of cannel, or
375lbs. per ton of tar.

The residual oil was a complicated mixture of aromatic hydrocarbons in which anthracene, phenanthrene, and other solids could still be detected.

The products from this tar compared favourably with those from average coal tar, except that the proportions are different. For example, there is a smaller yield of naphthalene, and a much larger one of anthracene from the tar of Hoo cannel. This difference is shown to a much greater extent by the fractions from the distillation of the second tar (750° C), the yield of anthracene here being exceptionally high.

We desire to place on record our thanks to T. Duxbury, Esq., Engineer and Manager of the Oldham Corporation Gas Works, for placing at our disposal an experimental gas plant.

We are indebted to Miss P. Wray for help during the preparation of the bulletin.

971

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

THE DETERMINATION OF THE CARBON DIOXIDE IN COAL

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PRICE
ONE SHILLING

BULLETIN 7
1920

PREFACE

The work carried out in this Bulletin has been submitted to the Lancashire and Cheshire Coal Research Association, and appeared of sufficient interest to warrant a wider circulation; it is, therefore, published for the information of any who may be interested.

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THE DETERMINATION OF THE CARBON DIOXIDE IN COAL

Literature.

A close examination of the literature shows that few results have been published of determinations of the amount of carbon dioxide evolved when coal is treated with acids. One reason for this probably lies in the fact that the ordinary methods for the estimation of carbon dioxide in carbonates are not easy to apply to coal. The amount of carbonates varies within wide limits in different seams, but as a rule is comparatively small.

The information is important for two main reasons: (1) It is not possible to ascertain the percentage of carbon in coal unless that occurring as carbonates, etc., is known. The value obtained in the ordinary method of determining carbon by combustion includes the carbon occurring both in the organic substance and in the carbonates, etc. If the exact percentage of organic carbon in the coal is required, that occurring in the carbonates must be determined, and deducted from the total carbon found by combustion. Certain coals contain up to 5 per cent. of substituted calcium carbonates, which is equivalent to approximately 0·5 per cent. of carbon. It follows that the percentage of organic carbon in the coal is 0·5 per cent. lower than that found by the combustion. This is of some importance when considering the calorific value of coal, as 0·5 per cent. of carbon is equivalent to 41·6 calories, or 74·8 B.T.U.'s per pound. In certain abnormal specimens of coal 30 per cent of calcium carbonate have been found.

(2) A knowledge of the amount of carbon dioxide occurring as carbonates is also an auxiliary means of obtaining an idea of the composition of the inorganic compounds present in coal. In a later paper, a number of analyses will be given of the white partings (ankerites) occurring in Lancashire seams. These compounds are fairly constant in composition in a particular seam ; if the composition of the ankerites is found by analysis, including the percentage of carbon dioxide present, it is possible to calculate approximately the composition of the particular compound contained in a sample of coal by a simple determination of the carbon dioxide.

The following processes for the determination of carbon dioxide in carbonates are in general use :—

Schroetter's apparatus, and various modifications may be expected to yield results within 1 per cent , when the percentage of carbon dioxide in the compound is high, and at least 1 gram is available. The method has been found to be useless for the determination of carbon dioxide in coal.

S. H. Collins (J.S.C.I., 1906, *25*, 519) describes an improved form of Scheibler's apparatus, in which the carbon dioxide evolved from carbonates by the action of acids is collected and measured. The method suffers from the inaccuracies inherent in any process where the measurement of small volumes of carbon dioxide are necessary. The equivalence of six sources of error is stated to be 1 per cent.

A method for the determination of small percentages of carbonates in such material as soil is described by Hall & Russell (J Chem. Soc., 1902, *81*, 83), who state that where the amount of calcium dioxide present is only about 0·5 per cent , the whole of the carbon dioxide produced when acid is added may remain dissolved in the reaction products.

The method most generally used is to decompose the carbonates with a suitable acid, and after purifying the carbon dioxide produced, to aspirate it through weighed potash bulbs. Unless the weight of carbon dioxide produced is considerable, the process is quite inaccurate, even when the precaution of counterpoising the potash is adopted , considerable variations in weight of the potash bulbs are possible from external causes.

A number of methods in which standard barium hydrate solution is used for the absorption of carbon dioxide have been described The general procedure advocated is to place the standard solution in some type of wash bottle, but the process has not been generally adopted, largely for the following reasons :

Barium hydrate is only comparatively slightly soluble in water, which necessitates the use of a large volume of solution, and consequently a cumbersome wash bottle ; the rate of absorption of carbon dioxide by barium hydrate solution is comparatively low, and consequently a slow stream of gas is essential in order to effect complete absorption. It is difficult, without introducing considerable elaboration to prevent the barium hydrate solution coming into contact with the air, or the breath of the experimenter during the manipulation of the process.

One of us* described an apparatus by means of which the rate of flow of a gas into an evacuated vessel could be controlled, and later† showed that the apparatus could be adopted for the accurate determination of carbon dioxide in carbonates. From the latter paper the following estimations may be quoted, as indicating the degree of accuracy attained by the method :—

Weight of calcite. Grams.	Carbon dioxide found. Grams.	Carbon dioxide calculated. Grams.
0·1310	0·0576	0·0575
0·1710	0·0754	0·0751
0 0826	0·0364	0 0363
0·3490	0·1526	0·1534
0·0785	0·0341	0·0345

Apparatus.

The apparatus required is shown in the diagram. (A) Is an efficient wash bottle containing caustic potash solution, which should be renewed frequently. If a rapid flow of air is required it should be supplemented by a second wash bottle. A test should be made to determine the efficiency of the wash bottle ; it is essential that the air passing through it should be free from carbon dioxide. (B) Is a decomposition flask as described by Lunge & Marchlewski, a Schroetters apparatus or any simple reaction flask. (C) Is a tube containing calcium chloride

This train of apparatus is all that is required when phosphoric acid is taken to decompose the carbonates in the coal. Phosphoric acid, as suggested by G. S. Morgan (Proc. Chem. Soc.

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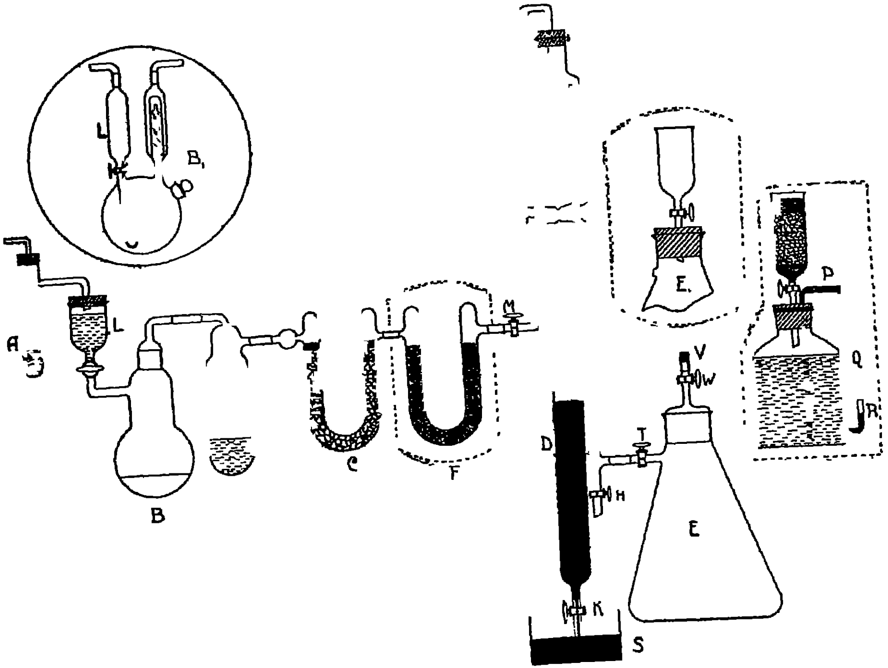
* Analyst, 1912, 37, 12. † Analyst, April, 1913.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1904, *20*, 167) yields results identical with those obtained with hydrochloric acid. When it is thought necessary to use hydrochloric acid, an additional absorption tube (F) must be introduced, containing alternate layers of glass wool and silver sulphate, in order to eliminate hydrochloric acid. (D) Is a special apparatus* the general form of which can be gathered from the diagram. It should not be less than 76 cms. (30 inches) in length, and have a diameter of ½ to 1 inch, but it should be as small as possible compatible with even working. The inner capillary tube should have an internal diameter of about $\frac{1}{16}$ of an inch, and be so arranged as to touch the walls and reach to the bottom of the larger tube. The taps of the apparatus should be well ground. In the reservoir (S) there should be sufficient mercury to fill the large tube. (E) Is an ordinary pressure flask, the capacity of which may be from one to three and a half litres (usually two and a half litres). The volume of air available for aspirating through the apparatus depends upon the capacity of this flask. Special flasks have been obtained with a ground stopper to which a funnel was sealed, but the arrangement shown which consists of a broad tube, having the inlet closed with a rubber stopper (V) has been found a most satisfactory method for the introduction of the barium hydrate solution into the flask.

Method of carrying out a determination.

The flask (E) is filled with fresh air and evacuated by means of an ordinary water pump. The carbon dioxide in the flask is reduced to such an amount as to be negligible. If the percentage of carbon dioxide in the air is known accurately, a correction may be applied for the carbon dioxide remaining in the flask. The evacuated flask is now attached to the special apparatus (D) in the manner shown in the drawing, the taps M, H and K being closed. The tap (T) is opened, and the tube of the outlet of the apparatus (D) is placed under the surface of the mercury in the reservoir (S). The tap (K) is then opened, and mercury is drawn into the tube (D) until the column is equivalent to the pressure in the evacuated flask; a record of the height of the column is made, and the tap (K) closed.

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* Analyst, 1912, 37, 12; Gas World, 22 Feb., 1913.

The sample of coal is pulverised to pass through a 1/90 mesh sieve, and from 0·5 to 5 grams are introduced into the decomposition flask (B). This is performed most conveniently by weighing the coal on a piece of smooth copper foil and brushing it into the flask, with a camel's hair brush. The coal is covered with about twice its volume (5 to 15 c c.m.) of distilled water, and is then gently heated, the contents being open to the air, until the water commences to boil, and maintained at a gentle simmer for about 20 minutes. By this means the occluded gases present in the coal are expelled (see page 13). The flask (B) is then assembled, connected to the train of apparatus, and hydrochloric acid (5 per cent.) or phosphoric acid (syrupy diluted 4 times) is placed in the cup (L). The acid is allowed to flow into the coal, the tap (K) is now opened, and (M) opened cautiously until air is drawn through the train of apparatus; the decomposition vessel is gently but efficiently agitated. The rate at which the air passes through the apparatus is carefully controlled, and should be kept constant. There is no necessity to alter the tap (M) once the rate at which the air flows through the vessel has been decided upon. After about 10 minutes the contents of the decomposition flask are gently heated, the temperature being maintained at about 50° C. for half an hour. The liquid is then raised to the boil, and kept at this temperature for an additional 10 minutes. Throughout the whole of this period air is allowed to sweep through the apparatus at the rate of about 2 litres per hour, and any carbon dioxide evolved from the coal is collected in the flask (E). The determination is now complete, and the flow of air is allowed to continue until the train has been completely swept through, or until the pressure in the flask has reached about 70 cms. The tap (T) is then closed, and the flask (E) disconnected. By attaching a freshly evacuated flask, the apparatus is ready for the next estimation.

Determination of the carbon dioxide.

The method of determination of the carbon dioxide in the flask by means of standard barium hydrate solution, is that described by Pettenkofer, the details of which are described in Lunge's Gas Analysis, but the following is the exact procedure adopted :—

Preparation and storage of the solution of barium hydrate.

The barium hydrate solution is prepared by adding 200 grams of barium hydrate, and 10 grams of barium chloride to one litre of distilled water After being allowed to settle, 60 c.c.m. of the clear supernatant liquid are transferred to an apparatus similar to the one shown on page 7 (P) and diluted to one litre with distilled water. This solution must be preserved from contact with the air, and the apparatus shown is convenient for this purpose. The containing bottle is fitted with an outlet syphon tube, having a narrow capillary (Q) ; this tube is fitted with a short length (2 inches) of india-rubber tubing (R). The use of a small capillary obviates the necessity of having to neglect the large volume of liquid which tubes of greater bore contain before the liquid actually contained in the vessel reaches the pipette. It also possesses the advantage that a pinch cock or bead valve is not required on the india-rubber tubing to prevent the liquid flowing out of the vessel; owing to the narrow capillary there is no tendency for either the liquid to be drawn back into the containing bottle or syphon, or out of it. The second hole in the stopper is fitted with a small tap funnel, which contains first a layer of glass wool, and then about 2 inches in depth of fresh soda lime. This is covered with a plug of glass wool, and finally the vessel is closed with a rubber stopper containing a single orifice. The barium hydrate solution has been found to keep very well under the above conditions, and no rapid change of titre will be experienced; at the same time it is desirable to carry out a blank determination upon the barium hydrate solution.

Method of titration.

The tip of the pipette is inserted into the rubber tubing (R) and the required volume of barium hydrate solution drawn off in the ordinary manner. In most of the experiments 50 c.c.m. were taken for the determination, and when the pipette was filled, the end of it was inserted directly into the rubber stopper (V) of the flask (E). The tap (W) of the flask was then opened gradually, when, owing to its contents being under reduced pressure, the liquid in the pipette is rapidly drawn into the flask. It will be seen that it is possible to repeat these conditions for each succeeding experiment, and as no gas is displaced during the introduction of the barium hydrate solution, one of the recognised sources of error associated with Pettenkofer's method is eliminated. The pipette is removed from the rubber stopper and any traces of barium hydrate remaining behind in the tube are washed into the flask with distilled water. The contents of the flask may then be brought to atmospheric pressure by connecting the outlet to a wash bottle containing caustic potash. The flask is allowed to stand for half an hour with occasional agitation ; one c.c.m. of phenolphthalein solution (one part in 250 c.c.m. of alcohol) is added, and the liquid rapidly titrated with hydrochloric acid (strength N/20 or N/40) until it becomes colourless. The first discharge of the pink colour is taken as the end-point of the titration. Frequently the pink colour returns, but this should be ignored. Where a large amount of carbon dioxide is present, and a distinct precipitate of barium hydrate is formed, it is desirable to shake the flask vigorously during the titration, in order to remove any barium hydrate which may be entangled (absorbed) in the precipitate.

The difference between the volume of hydrochloric acid required for the actual titration and that of the blank determination is the volume of acid equivalent to the carbon dioxide present in the flask, and consequently in the weight of coal taken for the determination ·—

$$2\ \text{H.Cl.} = \text{CO}_2$$

$$1\ \text{c.c.m. of N/40 H.Cl.} = \cdot 00055\ \text{gram CO}_2$$

The following shows the amount of carbon dioxide found in certain Lancashire coals, from which the white partings (ankerites) had not been separated :—

Seam	Weight of Coal.	Barium hydrate solution. c.c m.	Hydrochloric acid solution n/40 c c.m.	Carbon dioxide found grams.	Percent- of carbon dioxide in the Coal.
1. Mountain Mine	5·0	50·0	9·2	0·0252	0·50
2. Arley . ..	3·0	50·0	40·2	0·0054	0·18
3. Ravine ..	3·0	50·0	33·8	0·0107	0·36
4. Abnormal sample, I. ..	1·0	150·0	38·7	0·0685	6·85
5. Abnormal sample, II. ..	0·5	175·0	27·0	0·0916	18·32
6. Pemberton, 2ft.	0·5	50·0	42·8	0·0036	0·72
7. Garswood, 9ft.	0·5	50·0	45·8	0·0022	0·44
8. Hoo Cannel ..	0·5	50·0	32·4	0·0092	1·84

N/40 H.Cl (determinations 1 to 6) 1 c.c.m. = 0·00064 gram carbon dioxide.

N/40 H.Cl (determinations 7 and 8) 1 c.c.m. = 0·000524 gram carbon dioxide.

*Influence of prolonged treatment with water.**

If the period of heating the coal with water in order to eliminate the occluded gases is continued beyond 30 minutes, only a slight increase in the amount of carbon dioxide evolved could be detected, thus indicating that the period suggested (30 minutes) is adequate.

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* Bayley & Sinnatt

Five grams of coal boiled with 20 c.c.m. of water for 30 minutes :—

Carbon dioxide found = 0·09 per cent.

Allowed to simmer for 6 hours :—

Total carbon dioxide found = 0·10 per cent. of weight of coal.

Amount evolved during last 5½ hours = 0·01 per cent. of weight of coal.

*The influence of using different acids.**

The following determinations were carried out under identical conditions upon specimens from the same sample of coal, using hydrochloric acid and phosphoric acid. The results indicate that the two acids yield practically identical results by the method previously described.

Five grams of coal taken in each experiment :—

	Percentage of carbon dioxide.	
	Hydrochloric acid.	Phosphoric acid.
Coal No. 1	0·38	0·38
„ No. 2	0·27	0·26
„ No. 3	1·13	1·13
Fusain	0·61	0·56

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* Bayley & Sinnatt.

The above amounts were found when the coal was digested with the acid for three quarters of an hour. In the case of No. 1 coal the digestion was continued for further periods, with the following results :—

Period of digestion.	Carbon dioxide evolved. Hydrochloric acid.	Carbon dioxide evolved. Phosphoric acid.
First ¾ hour	0·38	0·38
Further 1½ hours	0·06	0·05
„ 4½ „	0·04	0·04

We wish to place on record our thanks to Miss P. Wray for help during the preparation of this bulletin.

972

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION.

THE INORGANIC CONSTITUENTS OF COAL WITH SPECIAL REFERENCE TO LANCASHIRE SEAMS.

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BULLETIN 8
1921

PREFACE

The demand for copies of the papers contained in this bulletin has exhausted the original supply of reprints.

The Lancashire and Cheshire Coal Research Association has, therefore, considered it desirable to republish the information in order to place it at the service of any who may be interested.

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Atherton.

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Jan. 15, 1921, *Vol. XL.*, *No.* 1, *pp.* 1T–4T]

THE INORGANIC CONSTITUENTS OF COAL WITH SPECIAL REFERENCE TO LANCASHIRE SEAMS.

This paper describes a stage in the study of the inorganic constituents of certain typical seams in the Lancashire coalfield, and records a part of an investigation of the various coals from a number of viewpoints The work has been carried out under the auspices of the Lancashire and Cheshire Coal Research Association.

It is well known that the coals in the Lancashire coalfield contain, as a rule, a low percentage of inherent ash. Of twenty distinct seams examined recently, none contained more than 6 per cent. of ash, whilst a great number contained less than 3 per cent. Bickershaw Yard coal contained as little as 0·8 per cent. The coals vary in properties from those which are practically non-caking to one (Mountain Mine) which possesses probably the highest caking power of any known coal, and yields a perfect metallurgical coke.

In distinguishing the coals the names in most common use have been adopted, but it must be recognised that other terms may be applied to the same seams in different localities.

For the purposes of this paper only the natural inorganic constituents of the seams have been considered Every care was taken in obtaining the samples on which the work was carried out. A solid pillar was cut from the whole seam, the cross-section of which was from 6 to 18in., according to the ease with which the coal could be handled The piece of coal was packed in a box and carried to the laboratory for examination.

The present investigation included the following objects :

To determine if any relationship could be established between the composition of the white partings (ankerites) and the ash produced when the coal is incinerated.

To attempt to trace the source of the carbon dioxide evolved when coal is treated with mineral acids

To investigate the form of combination in which iron exists in the coal substance.

The last subject is of interest in view of the fact that according to the work of Powell and Parr (Bulletin III, University of Illinois) the greater proportion of the iron present in certain American coals occurs in the form of pyrites, and with this fact is associated the assumption that the iron does not enter into the preliminary stages of the oxidation of coal

It would appear from the experiments described in the present paper that a proportion of the iron in Lancashire coals exists in the ferrous state, either in the white partings (or ankerites) or some other form of combination.

Most coal seams contain a proportion of white inorganic partings, of which no study has appeared in the literature It will be seen later that the material may be considered either as substituted calcium carbonate, or as dolomitised siderite The term ankerite, which is the one generally accepted in mineralogy for compounds having a similar constitution, has been adopted to distinguish the substance of the white partings

The ankerites occur in the form of sheets varying in thickness from ⅛in to a mere film, at right angles to the bedding plane and on the face of the coal, but also frequently on the end of the coal. The layer of material may be so thin as to be transparent, and its presence can only be detected by the fact that after being allowed to stand in the air the coal becomes covered with an opalescent film, consisting of oxidised ankerite. When ankerite occurs adjacent to a band of vitrain, it is frequently perfectly white in colour, whilst portions in contact with clarain or durain are comparatively dark, and impregnated with fine coal. It has been observed that a band of ankerite frequently terminates at a point where a layer of fusain occurs. The latter material is highly porous in nature, and it would appear that the ankerites have been deposited from a liquid medium which has travelled horizontally along the layer of fusain.

The ankerites form a distinct line of weakness in the coal, and if the latter is treated with dilute mineral acids, marked disintegration of the lumps is produced, owing to the decomposition of the compounds The whole of the specimens examined contained varying percentages of iron practically entirely in the ferrous condition, and it will be seen from the analyses that certain examples contained a distinct percentage of manganese.

Average specimens of the ankerites from a number of seams have been analysed, and the results are given in the following table :—

TABLE I.

Percentage composition of the white partings (ankerites).

	Lower Mountain Mine	Arley	Ravine Mine.	Sapling Mine.	Hoo Cannel.	Rushy Park.	King Mine.
	%	%	%	%	%	%	%
Calcium oxide ..	27·40	28·56	29·94	42·79	30·08	28·76	30·84
Magnesium oxide	13·33	11·51	16·15	0·41	11·18	8·74	5·76
Ferrous oxide ..	14·56	9·81	4·80	13·07	14·16	16·23	18·42
Manganese oxide.	—	0·82	1·11	—	—	0·59	0·31
Carbon dioxide ..	45·21	41·52	44·35	41·88	44·58	42·46	42·03
Silica	—	6·05	2·25	1·70	—	2·45	—
Ferric oxide ..	—	0·60	0·25	0·17	—	0·63	—
Pyrites	—	1·11	—	—	—	0·09	2·47
Equivalent to :—							
Calcium carbonate	48·93	51·00	53·14	76·41	53·70	51·36	55·08
Magnesium carbonate	28·30	24·07	33·65	0·66	23·48	18·28	12·10
Ferrous carbonate	23·46	15·81	8·40	21·68	22·82	26·18	29·68
Magnesium carbonate	—	1·33	1·80	—	—	0·96	0·50
Calcium sulphate.	—	—	0·44	—	—	—	—
Silica	—	6·05	2·25	1·70	—	2·45	—
Ferric oxide ..	—	0·60	0·25	0·17	—	0·63	—
Pyrites	—	1·11	—	—	—	0·09	2·47

Specimens of ankerite obtained from the different layers in certain seams differ considerably in composition, the following analyses show the greatest variation yet encountered :—

TABLE II.

Ankerite from seam 8ft thick.

	Top 15 in.	Bottom 7 in
	%	%
Silica	0·91	2·25
Calcium carbonate	52·09	53·14
Magnesium carbonate . .	29·74	33·65
Ferrous carbonate	16·15	8·40
Manganese carbonate	1·41	1·80
Ferric oxide	0·33	0·25
Calcium sulphate	nil	0·44

The compounds undergo oxidation on exposure to air and become covered with reddish-coloured ferric compounds.

The following analyses show the change in composition which occurred when a specimen of ankerite was exposed to the air in contact with the coal. It should be pointed out that the two specimens of ankerite were of necessity obtained at a slight distance from one another, and some small difference in chemical composition was detected :—

TABLE III.

	Sample freshly mined Colour : white.	Sample after exposure to air for 12 weeks. Colour : red
	%	%
Ferric iron	0·33	0·91
Silica	0·91	0·17
Ferrous oxide	9·29	10·58
Manganese oxide	0·87	1·08
Calcium oxide	29·17	29·31
Magnesium oxide	14·22	13·32
Carbon dioxide	44·67	44·74

The oxidation of the ankerites is influenced by the presence of carbon dioxide and water. As would be expected, the compounds are freely soluble in water in the presence of carbon dioxide, and the solution which results rapidly undergoes oxidation in the presence of air, with the precipitation of basic ferric compounds.

No accurate method of determining the percentage of ankerites in coal has been elaborated, but an approximate value was obtained for one sample of coal by crushing about 1,000 g. until it would pass through a sieve of 4's mesh, and separating all the ankerite that was visible by picking it out with forceps. The coal contained 4·2 per cent. of total ash and 3 per cent. of ankerite. The equivalent weight of ignited ankerite was 1·7 per cent.—*i.e.*, 40·5 per cent. of the ash was derived from the ankerite present.

Samples of the coals from which the ankerites described above were obtained were incinerated at a temperature of 900° C., and the resulting ashes were analysed with the following results.—

TABLE IV.

Composition of coal ashes.

	Lower Mountain Mine.	Arley	Ravine Mine.	Sapling Mine	Hoo Cannel	Rushy Park	King Mine.
	%	%	%	%	%	%	%
Silica ..	40·20	43·21	35·00	38·92	32·98	25·49	29·45
Ferric oxide ..	25·66	12·38	9·99	48·40	23·34	38·80	26·32
Alumina	25·41	28·47	31·58	3·68	26·86	20·61	29·53
Calcium oxide .	3·52	7·12	11·63	5·04	6·88	7·08	5·96
Magnesium oxide..	1·98	2·36	2·45	0·50	3·10	3·22	0·11
Sulphur trioxide	2·02	4·30	7·68	0·16	3·04	1·25	1·98
Alkalis and loss .	1·21	2·16	1·67	3·30	3·80	3·55	6·65
Percentage of ash in the coal ..	3·03	3·20	5·20	4·00	2·44	2·4	4·6

A comparison of the above results shows that the proportion of the various constituents occurring in the ash is not by any means parallel with that found in the ankerites.

The percentage of carbon dioxide evolved when the coals were treated with mineral acids was determined by a method described in Bulletin No 7 of the Lancashire and Cheshire Coal Research Association, from which the following results are extracted :—Mountain Mine, 0·57 per cent. CO_2, Arley, 0·18 per cent ; Ravine, 0·32 per cent. ; abnormal sample I., 6·85 per cent , Pemberton 2ft., 0·72 per cent , Garswood 9ft., 0·44 per cent ; Hoo cannel, 1·84 per cent ; Rushy Park, 0·76 per cent. ; Lower King, 0·77 per cent. ; Bickershaw Yard, 0·40 per cent

It was thought that it might be possible to calculate approximately the proportion of the ankerite in a particular seam by the above determination, but it was found that the percentage of carbon dioxide evolved was in excess of that required to combine with the whole of the bases occurring in the coal as ankerites.

The following example shows the result obtained if the carbon dioxide evolved is assumed to be derived solely from ankerites :—

TABLE V.

1 Lower Mountain Mine.

Ash = 3·03% Carbon dioxide = 0·57%

Constituents	Coal ash original analysis (100 g.)	Gross constituents of coal ash in 100 g. of coal	Ankerite analysis	Ignited ankerite equivalent to CO in 100 g. of coal. g.
Silica	40·20	1·218	—	—
Ferrous oxide ..	nil	—	14·56	—
Ferric oxide	25·66	0·779	—	0·314
Alumina	25·41	0·770	—	—
Manganese oxide (MnO)	—	—	—	—
Calcium oxide	3·52	0·106	27·40	0·533
Magnesium oxide ..	1·98	0·059	13·33	0·263
Carbon dioxide ..	—	—	45·20	—
Sulphur trioxide ..	2·02	0·061	—	—
Pyrites	—	—	—	—
Alkalis and loss ..	1·21	0·036	—	—

From the above consideration it will be clear that the amount of carbon dioxide evolved when coal is treated with mineral acids is more than sufficient to combine with the bases found in the inorganic constituents of the coal, and must be derived from other sources than ankerites.

The source of the carbon dioxide has not been traced accurately, but it will be shown later that a portion of the iron in coal probably occurs as ferrous carbonate, as distinct from that occurring in the ankerites The percentage of carbon dioxide is, however, of some interest from an analytical point of view Unless the amount of carbon occurring as carbon dioxide is deducted from that found by combustion of the coal, the percentage of organic carbon will be too high. The percentage of carbon dioxide should be deducted from the percentage of volatile organic matter, as presumably the whole of the carbon dioxide is evolved at a temperature of about 900° C In the case of the abnormal sample, the volatile organic matter determined was too high by 6·8 per cent

Mr. N. Simpkin, in collaboration with one of us, is continuing certain phases of the work, and has treated the coals with dilute hydrochloric acid, and determined the amount of iron which passes into solution , the total amount of iron present was also found.

It appeared desirable to ascertain what proportion of this iron occurred in the ferrous state, and specimens of the fresh coal were treated with hydrochloric acid (10 per cent) in an atmosphere of carbon dioxide. The excess of coal was removed by filtration in an atmosphere of carbon dioxide, and the amount of iron in the filtrate determined. It was found that the liquid contained a negligible quantity of iron in the ferric condition The iron in the ferrous condition was determined by oxidation and subsequent titration with a standardised solution of titanous chloride As this examination had to be performed on fresh samples of coal, the results are not exactly parallel with those previously quoted. The preliminary results are, however, strictly comparative, and are given in the following table :—

TABLE VI.

Coal	Total iron. %	Iron (ferrous) extracted with hydrochloric acid %	Iron (ferrous) extracted with hydrochloric acid Percentage of total iron
Rushy Park .	0·494	0·176	35·6
Lower Mountain Mine .	1·779	0·535	29·7
Arley	0·612	0·047	7·7
Ravine	1·379	0·205	11·9

The results quoted in this paper are of interest as indicating that a distinct percentage of the iron in coal, which differs widely in different seams, is present in the ferrous condition in the ankerites, and in some other form of combination, it does not necessarily follow that the iron extracted by means of hydrochloric acid is present in the coal in the ferrous condition, since it may have been produced by the action of coal upon ferric compounds. In certain cases distinct oxidation of the ankerites can be detected within a month of the seam being obtained from the mine.

From a chemical standpoint it will be of interest to obtain information as to the relative rates of oxidation of ankerites of different compositions, and the effect of this oxidation upon the oxidation of the coal substance and of pyrites. It is not obvious which type will most readily oxidise, but upon the behaviour of these compounds will depend the degree to which coals will weather, and as a corollary their properties during storage.

Oxidation obviously produces a change in volume or thickness of the sheets of ankerite, and consequently is a factor contributing towards the disintegration of masses of coal. When coal has been allowed to stand for extended periods, oxidation of sheets of ankerites has been observed at a considerable depth into the coal Up to the present no direct evidence has been obtained as to whether the primary heating of coal can be connected with the presence of ankerites, and the effect of manganese, etc , upon the general action of the ankerites At the same time, in view of the clearly recognised action of ferrous and manganese carbonates as catalysts, it appears of considerable interest to examine the subject in the light of the information described in this paper It would also appear that carbon dioxide may be an active agent in the oxidation of the compounds , we have found that ankerites are freely soluble in water containing carbon dioxide, and that the resulting solution rapidly undergoes oxidation, with precipitation of the iron in the form of ferric compounds. In a mass of coal evolution of carbon dioxide is known to take place, and in the presence of any excess of moisture, the conditions are such as to bring about the oxidation of the compounds, with carbon dioxide and water taking part in the reaction

When coal containing ankerites is burned, bands of residue from the ankerite will remain separate from the inherent ash of the coal, unless the temperature is sufficiently high to fuse the whole mass. The residual material from the ankerite will consist of highly infusible oxides It would follow that coal which has been broken to a small size will contain the ankerite and silicious coal ash in more intimate contact than when larger sizes are used

Analysts make a practice of quoting the colour of coal ashes, and it is well known that such ashes consist of a mixture of particles widely different in colour We therefore make it a rule to pulverise coal ashes to a fine powder (1 /200 mesh) in order to obtain an impression of the colour as a whole.

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION.

A NEW CHARACTERISTIC FOR COAL: THE AGGLUTINATING POWER CURVE

By F. S. SINNATT & A. GROUNDS.

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April 15, 1920, *vol. XXXIX., No* 7, *pp* 83T-85T.]

A NEW CHARACTERISTIC FOR COAL: THE AGGLUTINATING POWER CURVE.

This work is part of the investigation of Lancashire coals being carried out under the auspices of the Lancashire and Cheshire Coal Research Association.

The present paper contains a study of the agglutinating power of coal under certain special conditions, and affords an auxiliary means for the identification and valuation of coals, with especial reference to their caking qualities. Although the test for the agglutinating power of coal has been studied fairly completely by certain firms for industrial purposes, the literature of the subject is somewhat scanty, the following being the two chief contributions: Campredon * describes a method for measuring the caking value of coals by heating a standard weight of coal with varying weights of inert matter (Calais sand) in a platinum or porcelain crucible The test was repeated until the maximum amount of inert matter which could be sustained by a coal was found, the coal still yielding a coherent button of coke J. T Dunn † observed that, occasionally, coals of high ash value had given higher agglutinating values than coals of a similar nature but of low ash value, the latter coals being obviously much more suitable for the manufacture of coke He found that much more consistent results could be obtained by the use of anthracite in place of sand as the inert matter. The coal to be tested was passed through a ½mm. sieve (approximately 1/50 sieve), whilst the anthracite was graded from 1 mm. to ½ mm (*i e*, while it passed through a 1/25 sieve it would be retained by a 1/50 sieve). The proportion of the weight of inert

* *Comptes rend*, 1895; see this J., 1896, 186.
† This J., 1913, 397.

matter to the weight of coal was taken as a measure of the agglutinating power. In the discussion which followed this paper it was suggested that retort carbon might be substituted for anthracite, and one speaker also mentioned that particular care should be taken to specify the size of the anthracite Further, it was stated that the coking test should be carried out in a muffle, and not over a Bunsen burner, and that the period of carbonisation should be controlled It was considered that some definite mechanical means should be adopted to measure the strength of the resulting coke.

No further attempt, as far as we are aware, has been made since the publication of the above paper to standardise a method for determining the coking value of coals.

The temperature at which the coking or caking determination is carried out is usually lower than that at which the ash of coal becomes fusible, but there is a possibility (as suggested by Dunn) that the inorganic substances present in the coal may fuse during the carbonisation. It is well known that certain coals contain ferrous carbonate, and if the temperature at which the test is carried out is high, slight slagging may occur between the sand and the inorganic constituents of the coal. It is therefore desirable to choose an inert material which has no agglutinating power, either when heated alone, or when heated with coal. Further, a substance which does not give rise to the evolution of gaseous products is preferable, as these have a distinct influence upon the rate at which the volatile constituents of coal are eliminated from the sphere of the reacting mass. The greater the volume of gas evolved by the inert matter and the greater the proportion of the latter present, the shorter the period the volatile constituents are in contact with the coal during the carbonisation. For these reasons it is considered that sand and anthracite are not entirely suitable As it is desirable to measure only the caking power derived from the decomposition of the organic compounds present in the coal, which bind together the coke formed during the carbonisation, the inert material should resemble coke as far as possible. The inert material should not be porous, or it tends to absorb the binding or agglutinating substances produced during the carbonisation of the coal, the effect of which will be lost. Further, the particles of the material chosen should be spheroidal in shape, thus eliminating binding together of the substance by interlacing of the particles, either alone or when mixed with the coal or coke The substance finally chosen by us was pulverised electrode carbon, which appears to satisfy most of the above conditions. "Flame-arc" carbons should not be used, as these are impregnated with sodium and calcium salts, which might act as a flux for the ash of the coal, thus producing a binding effect and influencing the agglutinating value of the coal

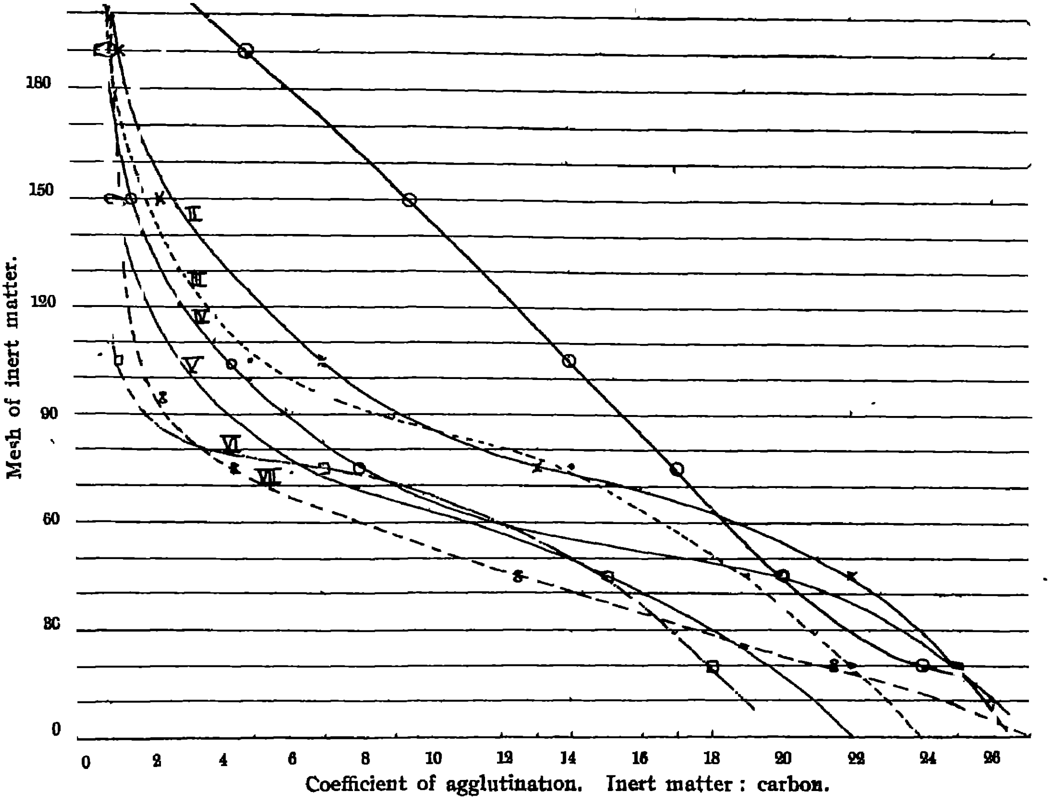
In order to study the influence of the degree of fineness of the powdered inert matter, a quantity of carefully graded electrode carbon was prepared; 14lb. of electrode carbon was pulverised so as to pass through a 1/10-mesh sieve. It was then intimately mixed and carefully sampled and analysed, with the following results:—Moisture, 0·17 per cent.; volatile matter, nil, ash, 1·4 per cent; carbon, 98·35 per cent. This material was then sifted through the following tiers of sieves: 1/10 to 1/30, 1/30 to 1/60; 1/60 to 1/90; 1/90 to 1/120; 1/120 to 1/180; 1/180 to 1/200; and through 1/200. Considerable difficulty was experienced in obtaining sieves of accurately sized mesh, and the above sizes had to be adopted finally, and the same material was used throughout. In our opinion, it is desirable to have the inert matter of such an approach to uniformity of fineness as will pass through, say 1/80 and be caught by a 1/90. The difference in size between the 1/60 and 1/90 is too large if great accuracy is aimed at, as it is possible for one specimen of the material to consist of a large proportion of 1/60 to 1/70 and a much smaller proportion of 1/80 to 1/90, and a second specimen to have the proportions reversed. In fact, the gradation in size of a 30's difference in mesh is not, in our opinion, sufficiently precise. It is hoped at a later date to repeat the experiments, using particles of inert matter more uniform in size.

A sample of Arley coal was carefully picked so as to be as free as possible from inorganic constituents, and the whole of the sample was ground to pass through a 1/90 mesh sieve Determinations of the agglutinating value were then made by mixing one unit of coal with increasing proportions of sand (graded 1/60 to 1/90), and adopting the standard American method for the determination of volatile matter in coal (*i e.*, 1 grm of coal or mixture is placed in a platinum crucible weighing 20–30 grms, on a silica triangle, over a Bunsen burner, and allowed to remain in the full flame for exactly seven minutes).

The coherence of the coke obtained from the volatile matter test was examined by removing the button and placing upon it a 100-grm weight, the surface of which was equal to that of the button obtained When the button crushed to powder under the pressure of the weight the maximum value was considered to have been attained The term "agglutinating value" is used to describe the proportion of the weight of inert matter to unit weight of coal With an Arley coal ground to pass through a 1/90 sieve, the agglutinating value with sand 1/60 to 1/90 was 15, while with gas carbon 1/60 to 1/90 it was 7·5. It would thus appear that the relative weights of sand and electrode carbon used are directly proportional to the specific gravities of the two substances, and that the 1 grm. of coal requires equal volumes of sand and electrode carbon. It was therefore concluded that the coefficient of agglutination of a coal is a function of the volume or surface of the inert material used This observation led us to examine the influence of the size of the particles of inert matter upon the agglutinating value of coals, and it was found that with decreasing size of particle the weight of inert material required to destroy the caking power of a coal was diminished. It was therefore decided to examine a number of typical Lancashire seams, and to plot as graphs the results of the agglutinating power determinations. The size of the inert matter experimented with was as previously stated, and in the graphs the size of the particle has been assumed to be the mean between the sieves used—*e g*, particles between 1/60 and 1/90 are taken as having an average size of 1/75 mesh

Average samples of coal were obtained from a number of different seams, each of which was treated in exactly the same manner The sample was ground till it would pass through a sieve of 1/90 mesh, and the agglutinating value determined Each experiment was carried out in exactly the same manner, and the reason for the adoption of the standard American method in this work was to make the results of greater interest, as it enables chemists who do not possess an electric furnace or a standard muffle, to compare the results with those we have obtained At a later date it is proposed to publish the results obtained by carbonising the coal in an electrically heated tube, the temperature of which is controlled by a thermo-couple The results for the different coals are given in the following table, and the figures are plotted in the diagram —

No	Name of coal	Fineness of electrode carbon.					
		1/180 to 1/200.	1/120 to 1/180	1/90 to 1/120	1/60 to 1/90.	1/30 to 1/60	1/10 to 1/30
		Weight of electrode carbon per one unit of coal					
1	Mountain Mine	5·0	9·5	14·0	17·0	20·0	24·0
2	Garswood, 9 ft. ..	1·5	2·5	7·0	13·0	22·0	25·0
3	Bacon Mine, tops ..	1·2	2·5	5·0	14·0	19·0	22·0
4	Arley .	1·2	1·7	4·5	8·0	20·0	25·0
5	Ravine, tops .	1·0	1·3	3·0	7·0	15·0	19·5
6	Hell Hole, middles	1·0	1·1	1·3	7·0	15·0	18·0
7	Chanters, 4ft. ..	1·0	1·3	1·5	4·5	12·5	21·5


Mesh of inert matter.
0
30
60
90
120
150
180
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Coefficient of agglutination. Inert matter : carbon.
II
III
IV
V
VI
VII

The graph for No 1, which is practically a straight line, shows no evidence of any bend when the size of the inert matter becomes extremely small This is interesting in view of the fact that No 1 coal yields by far the most voluminous and perfect foundry coke of any of those examined

An examination of the curves leads to one point of importance, namely, that not only does the fundamental property of caking of different coals vary considerably, but the property is influenced by the degree of fineness of the inert substance until, when inert material finer than 1/90 mesh is taken, the caking property of the coal may be entirely destroyed by less than its own weight of inert matter Attempts were made to determine the agglutinating value with less than one unit of inert matter, but the results have not, up to the present, led to a satisfactory conclusion, and are not included in this paper There appears to be no reasonable objection to the conclusion that, if finer inert particles were used than those already experimented upon, the weight of inert material required would be reduced. It is suggested that the most satisfactory manner of determining the agglutinating power of coal is to prepare a graph, showing the relationship between the size of mesh of the inert matter used, and of the weight required to destroy the caking power of a unit weight of coal. This we have called the " agglutination curve " , it will be seen, however, that this determination is rather laborious, and as an alternative we suggest that the agglutinating powers of coal should be measured by the fineness of the inert matter required to destroy its caking properties. The manner of carrying out this test would be to mix one part of coal intimately with, we suggest, three parts of inert material, the size of particle of which should be varied, until the coal will no longer yield a coherent button with the inert matter The caking index would then be expressed in the degree of fineness of the inert matter—*e g* , one coal would be, say, 1/200 mesh, the next would be 1/75. It has been found by us that the size of the particle of inert matter does not influence the percentage of volatile organic matter evolved when the coal is heated as shown by the following series of experiments In these experiments one unit of coal, powdered to pass through a 1/60 sieve and be caught by a 1/90 mesh sieve, was mixed with four units of inert matter (electrode carbon) of the following degrees of fineness and one grm of the resulting mixture was carbonised under constant conditions :—

(Size of inert matter electrode carbon)	* Percentage of volatile organic matter evolved, calculated on coal taken.
1/10—1/30	28 6
1/30—1/60	29·0
1/60—1/90	29 4
1/100—1/200	29 4
1/200 and finer.	29 6

* Mean of three determinations for each experiment.

It can hardly be hoped to discuss the subject from any but a limited number of aspects in this paper, but the following points may be considered.

It is well known that during the washing of coal a considerable proportion of fine material is produced, part of which contains a high percentage of inorganic matter and fusain. This material has to be disposed of in one form or another, and where the intention is to manufacture coke the fine material or dant is distributed throughout the mass of the coal. It would appear that the addition of this fine dant, which usually possesses a low caking value, and in some cases is entirely without caking properties, although produced from a caking coal, will lead to a distinct difference in the caking value of the coal itself. Further, it is clearly important that the fine material should be mixed throughout the mass of the coal as perfectly as possible, as its accumulation in certain parts of the masses of coal would lead to the production of coke possessing distinct lines of weakness, due to the presence of sufficient finely-divided inert matter to render the coal at this particular point entirely non-caking

The above observation applies to some extent to the processes in which coal and coke are mixed for use during steam raising, but it would seem that the addition of a small proportion of very finely-divided coke might have a distinctly beneficial effect in reducing the caking power of a coal which otherwise might be unsuitable for steam raising.

The influence of the inert matter also arises in the stone-dusting of mines; finely pulverised stone dust is sprayed into mines with a view to eliminate any chance of the fine coal dust in the mine exploding; the mixture of coal and stone dust deposits on the floor, walls, and roofs in the pit. The addition of a small proportion of this very fine material to caking coals would cause the coal to act as a non-caking coal

It should be mentioned that the figures given in this paper were obtained under conditions which were as uniform as possible, and represent the agglutination curves of the coals at one particular temperature. It appears that the shape of the curves may vary considerably with alterations in the temperature, and it is proposed at a later date to prepare curves for certain characteristic seams at a series of constant temperatures.

We wish to place on record our thanks to Miss P. WRAY for help during the preparation of the papers contained in this bulletin.

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION

STONE DUSTING OF MINES

PART I,

SAMPLING AND ANALYSIS

F. S. SINNATT, M.B.E.
M.Sc (Tech), F.I C, M.I Min E.
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AND
A. McCULLOCH, A.I.C

973

BULLETIN 9
1921

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STONE DUSTING OF MINES.

PART I.

SAMPLING & ANALYSIS OF MINE DUST

Introduction.

No exact interpretation of the new regulations (Statutory Rules & Orders, 1920, No 1423, Part I Section 62) with reference to stonedusting is available, and the meaning of paragraph 4 is not clear.

At the request of a number of collieries the following brief description of a method of sampling, and the analysis of the mine dust has been prepared.

Representative sampling.

The Coal Mines Act (Statutory Rules & Orders, 1920, No. 1423, Part I. Section 62) states:

"4. For the purpose of testing the composition of the dust mixture in any part of a road, the following procedure shall be adopted.—

(*a*) Representative samples of the dust shall be collected from the floor, roof and sides, over an area of road not less than 50 yds in length

(*b*) The samples collected shall be well mixed and a portion of the mixture shall be sieved through a piece of metallic gauze having a mesh of 28 to the linear inch

(*c*) A weighed quantity of the dust which has passed through the sieve shall be dried at 212° Fahrenheit, and the weight lost shall be reckoned as moisture. The sample shall then be brought to a red heat in an open vessel until it no longer loses weight. The weight so lost by incineration shall be reckoned as combustible matter for the purposes of the test "

In the absence of an official interpretation of sub-paragraphs (*a*) and (*b*) above, the following method of sampling is suggested as a means of obtaining a representative sample of the dust from the floor, roof and sides.

In any particular length of 50 yds a sample is obtained of the dust from the floor, roof and sides, by brushing the whole of it off a width of about 4 inches into a metal box, at intervals of say 10 yds It is convenient to have the box fitted with a lid, which should be so arranged that when the box is open the lid protects the contents from the force of the air current, and thus prevents the fine dust being carried forward and lost as it is swept into the box. With such an arrangement it is possible to sweep a band of dust from the roof, sides and floor, without undue loss of any portion of it. An ordinary painter's brush about 4 inches wide is suitable for this purpose.

The five samples collected from the 50 yds are collected in the box, or if necessary transferred to a larger receptacle having a lid , the whole is intimately mixed by shaking, and a portion taken out and sieved through lamp gauze (28 meshes to the linear inch). The material which passes through is collected in a small tin box (a suitable size is 2½ inches in diameter and ⅜ inch deep), having a tightly fitting lid. Each box should be numbered, and when samples are submitted for analysis a list should be kept showing the position in the mine, the date and the sampler's name

The above method gives what may be termed a "perimeter sample," and may be considered to be representative of the 50 yds. of road over which it is taken.

In place of the brush, a broad palette knife or small shovel may be used for obtaining the samples, but there is a tendency to remove the materials of which the roof, sides and floor are composed, and thus vitiate the results Little variation will be found to occur in the moisture content of the samples if enclosed in metal boxes. For many purposes the samples may be collected in stout envelopes, provided they are not kept too long before being analysed

TESTING THE SAMPLE (para 4c)

If it is necessary to store a sample for any length of time it should be kept in a position where the temperature is uniform, and the humidity of the air is fairly constant, and should be contained in an air-tight tin

Apparatus required

A sieve of ordinary lamp gauze, 28 meshes to the linear inch.

A number of circular silica dishes, 2 inches in diameter, ¼ to ½ inch in depth

Bunsen burners and a small gas-heated muffle, or an electrical muffle

Tripod stands. Pipeclay triangles. Crucible tongs.

A balance, which should be sufficiently delicate to turn with about 1 milligram A glass cover is not necessary, but is a distinct advantage as it preserves the balance and keeps it delicate. A box of weights

A desiccator, and calcium chloride, for use in desiccator.

An oven heated to 212°F An air oven heated by means of a bunsen or an oven heated by steam It should contain a thermometer to indicate the temperature.

The total cost of the above apparatus is from £15 to £20, according to the type of the balance.

Determination of Moisture

A silica dish is weighed (1) and into it is brought a portion of the mine dust the dish and its contents being then weighed (2) The weight of the mine dust should be from 2 to 3 grams The dish is placed in an air-oven, which has previously been heated to 212°F (100°C) It is allowed to remain in the oven for one hour, and whilst still hot is transferred to a desiccator. The atmosphere in the desiccator is perfectly dry, with the result that whilst the dust is cooling it does not re-absorb water. When the sample has become quite cold it is removed from the desiccator and re-weighed (3) as rapidly as possible The loss in weight is the percentage of moisture in the mine dust. (Mines Act, para 4c)

Example

Weight of dish and mine dust (2) ..	15.43	grams.
Weight of dish alone (1)	10.43	,,
Weight of mine dust	5.00	,,

After drying in oven for one hour at 212°F.

Weight of dish and mine dust (2) ..	15.43	,,
Weight of dish and mine dust after drying (3)	15.27	,,
Loss in weight (moisture)	0.16	,,

Percentage of moisture = 0.16 x 100 - 3.2%

Determination of combustible matter

The dish and its contents from the above determination of moisture are then placed on a triangle over a bunsen burner, and then in a muffle, and heated first slowly and then as strongly as possible, until no black particles can be detected; the heating will require at least an hour. When free from black specks the dish is cooled and weighed again, and the loss in weight is the combustible matter mentioned in the Mines Act

Example.

Weight of dish and mine dust ..	15.43 grams.
Weight of dish alone	10 43 ,,
Weight of mine dust	5 00 ,,

The mine dust is then incinerated until nothing but ash remains .

Weight of dish and mine dust after drying at 212°F.	15.27 grams.
Weight of dish and ash	14.00 ,,
Loss by incineration ≐ combustible matter	1.27 ,,

$$\text{Percentage of combustible matter} = \frac{1.27 \times 100}{5} = 25.4$$

Summary.

Analysis of stone dust.

Moisture	3.20%
Combustible matter	25.4%
Ash	71.4%

9714

THE LANCASHIRE & CHESHIRE
COAL RESEARCH ASSOCIATION.

THE DETERMINATION OF THE CALORIFIC VALUE OF COAL

By F. S. SINNATT, M.B.E.
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(Director of Research to the Association)
and
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BULLETIN 10
1921

PREFACE.

The present bulletin has been prepared in response to a number of enquiries which have been received for a detailed description of the method of determining the calorific value of coal used by the Research Association

R. A. BURROWS.

President of the Lancashire and
Cheshire Coal Research Association,

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Atherton,

THE CALORIFIC VALUE OF COAL.

In the present bulletin no attempt has been made to deal with the subject of calorimetry in a general manner; it is limited to a brief description of the actual routine methods used by the authors for the determination of the calorific (thermal) value of coal On this account it has not been considered necessary to introduce references to the original literature and if greater details are required the work by J H Coste and E R. Andrews* is recommended.

It is recognised that other calorimeters than those mentioned will, under proper conditions, yield results possessing the same order of accuracy

At a later date it is proposed to issue separate bulletins containing (a) a description of the chief seams in the Lancashire coal field including the calorific value of the different coals and (b) an attempt to frame a logical system for the purchase of coal based upon its calorific and other values

Units of heat

The calorific (thermal) value of coal is expressed in the following units .—

British Thermal Units (B Th U) per pound A British Thermal Unit is the quantity of heat which raises the temperature of one pound of water one degree Fahrenheit

Calories per gram A Calorie is the quantity of heat which raises the temperature of one kilogram of water one degree centigrade (15·5 to 16·5°C.)

In terms of the number of pounds of water, the heat evolved by burning one pound of coal, will convert from water at 100°C. (212°F.) into steam at 100°C (212°F) (i e calorific value of the coal in B Th.Us or Calories divided by the latent heat of steam in B.Th Us (970) or Calories (539)).

---

*Fuel. Examination and Thermal Value (Griffin).

In order to convert Calories per gram. into B.Th Us per pound the former value is multiplied by the constant 1·8

Gross and net calorific value.

It should be recognised that when coal is burned in air, the products of combustion as a rule leave the system at a temperature higher than the boiling point of water and the steam produced by the combustion of the hydrogen in the coal is not condensed The latent heat of the steam is not recovered as part of the heat evolved by the combustion of the coal In calorimeters the steam is condensed and the temperature reduced to about 20°C. before the products of combustion are allowed to escape from the instrument, and the heating value as determined, is therefore, higher than can be recovered from the coal in practice This is called the gross calorific value of the coal. If the heat evolved by the condensation of the steam and cooling the water produced by the oxidation of the hydrogen in the coal, is deducted from the gross value, the result is the "net" calorific value of the coal From the point of view of the consumer the "net" value is a truer representation of the calorific value of the coal, than that given by the calorimeter The following is an example of the difference to be expected (assuming the latent heat of steam to be 970 B Th.U. and temperature 68°F.)

Percentage of Hydrogen in coal, 5·0.

Gross calorific value	14,700 B Th U. per lb
Nett ,, ,,	14,199 ,, ,,

The calculation of the calorific value

A number of formulæ have been suggested for the calculation of the calorific value from the results obtained by the chemical analysis of coal Two types of formulæ are common, based upon —

1. The ultimate analysis of the coal.
2. The proximate analysis of coal.

Calculation of the calorific value from the ultimate analysis.

Formulæ requiring the results of the ultimate analysis of coal suffer from the distinct disadvantage that the analysis must have been completed before the formula can be applied. Further as the results of the ultimate analyses cannot be assumed to be accurate within narrow limits (see Bulletin 4, page 36) the value given by such formulæ is not as accurate as that obtained in the bomb calorimeter

The formula originally suggested by Dulong is as follows :—

$$C\,V = \frac{1}{100}\left(8080\ C. + 34{,}460\ \left(H\ \frac{O}{8}\right) + 2250\ S\right).$$

This has been modified by numerous experimentors, and Gray and Robertson (J S. C I.1904, 23. 704), adopted the following :—

$$C.V = \frac{1}{100}\left\{8140\ C. + 34500\left(H - \frac{(O+N)-1}{8}\right) - 2220S\right\}.$$

Where C H. O. N. S = percentage of carbon, hydrogen, oxygen, nitrogen, sulphur in the coal

In order that such formulæ should yield accurate results, it must be assumed (1) that the ultimate analysis of coal is an accurate reflex of its composition (see Bulletin 4. Notes on Coal Analysis, page 36) ; (2) that the elements are present in the coal as such, and not in chemical combination It is recognised that these conditions do not exist practically and that such formulæ yield only approximate results.

Formulæ based upon the results of the proximate analysis of coal.

A number of formulæ are available for the calculation of the calorific value from the results obtained in the proximate analysis. Such formulæ are valuable when the same seam of coal is being dealt with continually. It is well known that particular seams of coal occasionally show small variations in composition throughout the mass of the seam, *i e.* the composition of the actual organic coal substance is uniform in character. Where such a seam as this is being examined, formulæ of the type under discussion are extremely accurate. It should also be recognised that other seams of coal vary widely in composition. In this case formulæ of the present type yield results which are worthless Parr and Wheeler (U S. Geological Survey, 1909, Bulletin 37) express views which have been widely held that the organic or mother substance of coal is frequently uniform in character

The recent work of Stopes, Wheeler, Lessing and one of the authors indicate that wide divergencies in analytical values are to be expected for the four constituents of banded bituminous coal (vitrain, clarain, durain and fusain) The chemical composition of coal will vary with the proportions of these constituents present.

One formula suggested for the calculation of the calorific value of coal from the values obtained in the proximate analysis is that devised by M Goutal (Comptes Rend, 135, 12, 477–79). This is based upon determinations of the calorific value of six hundred different samples of coal, and yields values which agree with those obtained in the bomb calorimeter to within 1%

Goutal's formula

Calorific value in Calories $=82C+aV$

Where 'C' is the percentage of "fixed carbon" 'V' is the percentage of volatile matter less moisture, and 'a' is a constant which depends upon the percentage of volatile matter calculated upon the basis which eliminates ash and moisture $\left(\frac{100\times V}{C+V}\right)$

The following table contains the values for 'a' for corresponding values of $\frac{100\times V}{C+V}$

$\frac{100\times V}{C+V}$	a	$\frac{100\times V}{C+V}$	a	$\frac{100\times V}{C+V}$	a
1 to 4	100	16	115	29	99
		17	113	30	98
5	145	18	112	31	97
6	142	19	110	32	97
7	139	20	109	33	96
8	136	21	108	34	95
9	133	22	107	35	94
10	130	23	105	36	91
11	127	24	104	37	88
12	124	25	103	38	85
13	122	26	102	39	82
14	120	27	101	40	80
15	117	28	100		

When a particular seam or mixture of seams is being examined the accuracy of formulæ of the type of Goutal's may be increased by a determination of the calorific value on one particular sample in a bomb calorimeter From these results the value for 'a' which must be assumed to be constant for a particular seam may be calculated This value is then substituted in Goutal's equation when applying the formula for the determination of the calorific value of subsequent samples from the same source

Example of the application of Goutal's formula —

Approximate analysis of Coal

Moisture	1·9
Ash	3·3
Volatile Matter (less moisture) ..	33 4 (V)
" Fixed Carbon " (Coke less ash)	61 4 (C)

$$\frac{100\times V}{C+V}=35\cdot2 \quad \therefore \ a=94 \text{ (see table above)}$$

Calorific Value in Calories

$$=82\times61\cdot4+94\times33\cdot4=8179 \text{ Cals.}$$
$$=14{,}720 \text{ B Th.Us}$$

As determined in bomb calorimeter

$$=14{,}740 \text{ B Th.Us.}$$

When the sample of coal contains calcium or substituted calcium carbonates, formulæ of the type of Goutal's are worthless for the calculation of the calorific value. The carbonates undergo decomposition when ignited and give rise to inaccurate figures for the volatile matter. In the case of certain samples of coal which have been examined the carbon dioxide evolved by treatment with mineral acid was found to be as high as 18%

The determination of the calorific value.

Many methods have been described for the determination of the calorific value of coal; it is only proposed to deal with two types of calorimeters which exhibit characteristic features The two types are .—

(1) The sodium peroxide calorimeter.

(2) The bomb calorimeter.

In mentioning the names of these instruments, it is not intended to suggest that they are better than many other instruments on the market The types are used in the laboratories of the Association and have given reasonable accuracy and service

The sodium peroxide calorimeter (*Roland Wild*)*

The makers supply a comprehensive description of the method of using the apparatus The general construction of the instrument may be gathered from the drawing

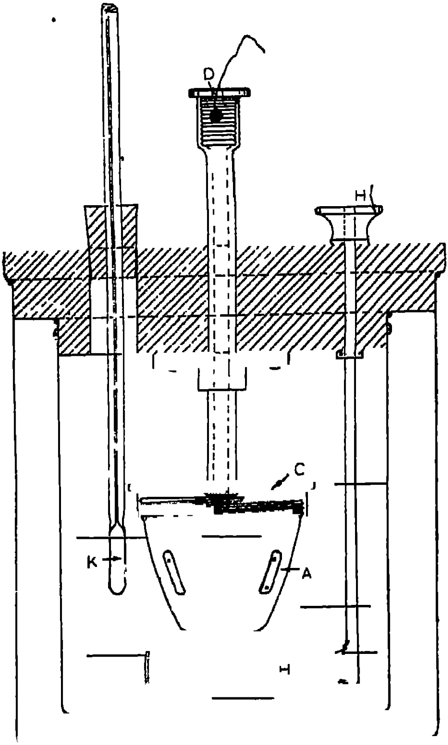

FIG I

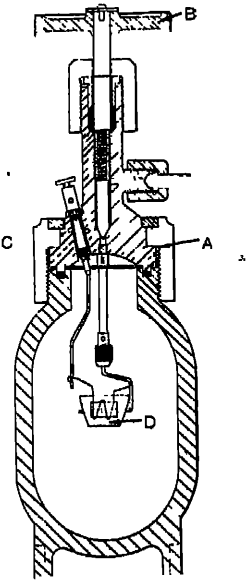

FIG. 2

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*Messrs Alexander Wright & Co , Ltd., Victoria Street, Westminster.

(Fig 1), (a) is a nickel crucible provided with lugs by which it may be screwed into the conduit (c) which is fitted with a small ball valve (d).

(NOTE. This valve is perhaps the weakest part of the instrument and has been replaced on one instrument by a brass tap with a bore $\frac{3}{16}$ inch, which has proved especially effective)

The water equivalent of each instrument is supplied by the makers and is generally about 75 grams but should be checked by an actual determination on a sample of coal of known calorific value; 925 grams of water are placed in the inner vessel. 0·73 gram of the coal, pulverised to a degree of fineness which varies with the type of coal under examination is intimately mixed with 12 to 14 grams of granulated sodium peroxide Sodium peroxide in the form of a fine powder should not be used. The mixture is brought into the nickel crucible (a), which is then screwed into the cap until a gas tight joint is formed with the rubber washer. The thermometer (Fahrenheit) is now arranged in position, with its bulb (k) on a level with the base of the crucible, the instrument is assembled and placed in a position in which a uniform temperature is maintained. The water is agitated by means of the stirrer (h) until the temperature recorded on the thermometer is constant. A piece of nickel wire about $\frac{1}{16}$ inch in diameter, and $\frac{1}{2}$ inch in length is heated to bright red heat in a bunsen burner, and whilst hot is allowed to fall through the valve (d) which is at once closed. The hot nickel wire ignites the coal, which continues to burn in the oxygen derived from the sodium peroxide. Throughout the operation the water in the vessel should be agitated by means of the stirrer. The difference in temperature between that recorded in the instrument before ignition, and the highest temperature reached during the determination, is the rise in temperature to be noted. This value multiplied by 1,000 (925 grams of water plus 75 grams) is the calorific value in British Thermal Units per lb. of coal. 27% of the total heat evolved by the combustion of the coal is derived from the reactions occurring between the products of combustion (water, carbon dioxide, etc) and the sodium peroxide This accounts for the fact that only 0·73 gram of coal is used.

On the completion of the test, the instrument should be washed out with water and dilute acetic acid, and then thoroughly dried, finally a small quantity of vaseline should be applied to the thread of the screw on the crucible

It will be gathered that the instrument is easy to manipulate and is empirical in character, its accuracy may be enhanced by carrying out a series of determinations upon various coals, the calorific value of which has been found in a bomb calorimeter By this means the water equivalent of the instrument may be ascertained for coals of different types. These constants are then introduced whenever coal of a particular nature has to be examined in the instrument. It should be emphasised that the degree of fineness of the coal must be chosen with care, otherwise the combustion may proceed with explosive violence

The fused mass remaining in the crucible contains the sulphur from the coal in the form of sodium sulphate It may be washed out into a vessel and treated in the usual manner for the estimation of sulphuric acid* (See Parr J, Ind. Eng. Chem, 1919, ii 230)

The bomb calorimeter.

It is not proposed to describe the elaborate precautions which have been suggested with a view to increasing the delicacy of the determination of the calorific value of coal in a bomb calorimeter, the errors associated with the various details will, however, be commented upon. A description of the methods adopted in the laboratories of the Association is given, to indicate the precautions that are considered necessary in order to standardise the errors of the experiment.

The general arrangement of the calorimeter, and the method of stirring, lighting and reading, may be gathered from Figure 3

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*See Bulletin 4, Notes on Coal Analysis, by F S Sinnatt.

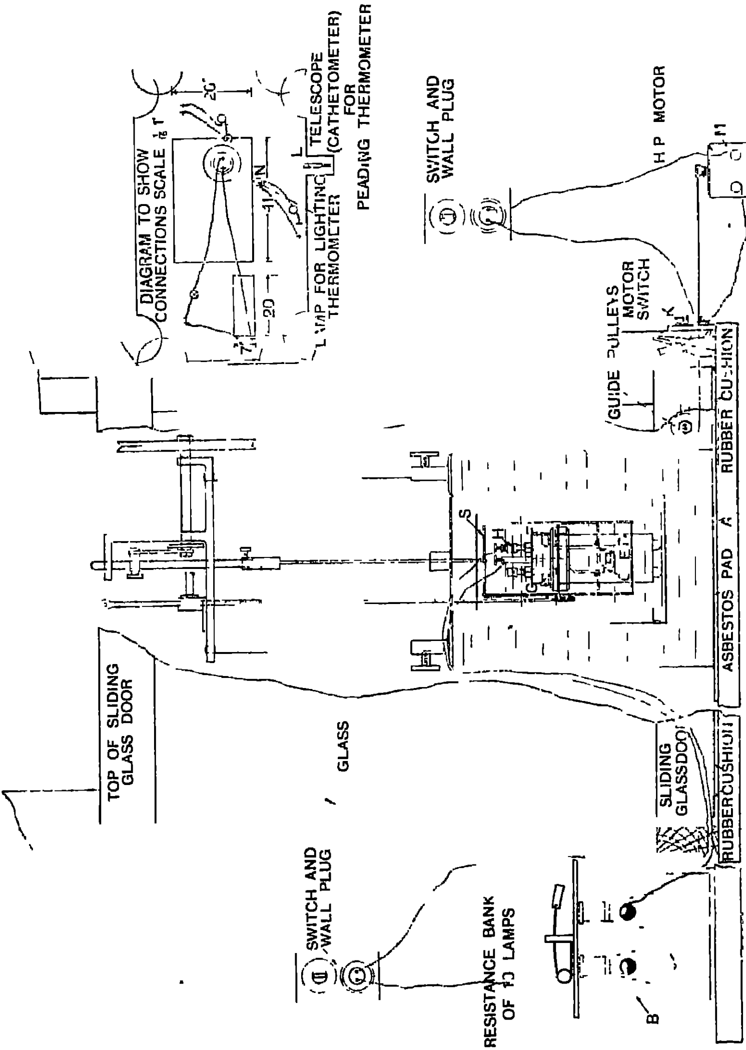
DIAGRAM TO SHOW CONNECTIONS SCALE 1/16"
20"
11
20
N
L
T
TELESCOPE (CATHETOMETER) FOR PEADING THERMOMETER
LAMP FOR LIGHTING THERMOMETER
SWITCH AND WALL PLUG
H P MOTOR
M
GUIDE PULLEYS
MOTOR SWITCH
K
RUBBER CUSHION
ASBESTOS PAD
A
S
H
E
G
TOP OF SLIDING GLASS DOOR
GLASS
SLIDING GLASSDOOR
RUBBERCUSHION
SWITCH AND WALL PLUG
RESISTANCE BANK OF 10 LAMPS
B

FIG. 3

The calorimeter vessel is placed on a circular piece of thick asbestos board (a) to reduce the conduction from the instrument, and stands on a slate slab in the centre of a chamber 3 feet wide by 2 feet deep by 4 feet high, to which is fitted a sliding glass door made airtight by means of a rubber cushion at the lower end The chamber is fitted into the brickwork of an inside wall, and in it a constant temperature is recorded. By raising the glass door, the manipulation required during the determination is effected Before the actual estimation is commenced, the glass door is closed, and the instrument isolated from the laboratory The switch for the stirrer (k) and the motor (m) for driving the stirrer are outside the chamber in order to eliminate any heating from this source. The bank of lamps (b) required for firing the wire for igniting the charge is at a distance from the calorimeter, the thermometer is illuminated from the outside by means of an electric lamp (n) and the reading is made through the window of the chamber by means of a telescope or cathetometer (l) placed at about 2 feet from the calorimeter chamber

Details of the apparatus

The calorimeter (copper) containing 19 litres of water, remains in the calorimeter chamber permanently, and is consequently always at the temperature of the chamber.

The thermometer

The thermometer is of the solid stem type, having a range between 15° and 23°C. It is divided into 1/100ths and can be read to 1/1000°C In view of the short range it is not possible to obtain an easy standard against which the thermometer may be checked, and it is, therefore, advisable to obtain one which has been standardised at the National Physical Laboratory. (Beckmann thermometers are considered too fragile for ordinary determinations.)

The stirrer.

The stirrer (s) (perforated horse-shoe shape) is arranged so that no part of it except the rod projects above the water in the calorimeter vessel, in order to reduce evaporation to the lowest limits. The rate of the stirrer is 100 strokes to the minute It is driven by a separate motor (m)

The bomb.

The construction of the Mahler-Kroecker bomb is shown in Figure 3 It will be seen that inlet and outlet valves are provided, designed originally to admit of the estimation of the carbon dioxide and water produced during the determination. Owing to the fact that sulphuric acid and nitric acid are both formed in the oxidation of coal, it is not possible to determine the water formed. Further, the determination of carbon dioxide as part of the determination of the calorific value of coal is not economical If water is introduced into the bomb, previous to the determination, it is troublesome to expel the carbon dioxide from the liquid into a weighed potash bulb These considerations have led us to use the bomb calorimeter solely for the determination of the calorific value.

The lid or head of the bomb is provided with a lead washer, and when screwed to the bomb forms a perfectly gas-tight joint. The ease with which the head can be unscrewed at the completion of a determination depends largely upon the application of a trace of lubricant (vaseline of high melting point) in such a manner that none is allowed inside the bomb In order to protect the enamel at the bottom of the bomb from specks of hot wire, it is covered with a thin sheet of platinum foil This does not interfere with the efficient washing of the bomb in order to determine the nitric and sulphuric acids formed during the process Certain precautions will be mentioned later in the method of using the pin valves during the actual manipulation of the bomb, but it may be pointed out that especial care and cleanliness are necessary in order to keep them in good working condition. The valves are removed and thoroughly washed with water and dried before putting the calorimeter on one side The inside of the head of the bomb is gold plated; this gold plate rapidly wears off The lid of one bomb has been covered with thin platinum foil.

Briquette-making press.

The coal is pulverised to pass through a 1/90 mesh sieve and may be made into a briquette in a special press supplied with the apparatus This press admits of the wire used for starting the combustion being bound into the coal during the moulding When it is found that the coal does not readily form a briquette it may be mixed with a known weight of pure benzoic acid or with a sample of coal which readily forms a briquette, the calorific value of which is known. By embedding the firing wire in the coal, very few misfires are experienced, whilst the tendency of the iron wire to be thrown on to the enamel of the tomb is reduced to a minimum In 100 determinations only 8 beads of iron were found on the enamel

It is not essential to make the coal into a briquette, but it may be weighed into a silica or platinum crucible and the wire for firing arranged in it in the form of a short spiral. The main objection to this method is that misfires are more frequent than when the coal is made into a briquette.

Wire for firing.

Platinum wire (0 0035 inch diameter) is preferred to iron wire, although the latter has been largely used in the Mahler-Kroecker bomb

Oxygen.

The cost of oxygen is a considerable item, and in order to minimise waste, at least two cylinders should be in operation at the same time, one being used as a low pressure, and the second as a high pressure cylinder. The bomb is first connected to the low pressure cylinder, and filled to the maximum pressure in the cylinder, it is then closed and connected to the high pressure cylinder and the pressure allowed to rise to 25 atmospheres. By this means it is possible to exhaust each cylinder of oxygen.

Water equivalent of the apparatus.

In determining the water equivalent of the bomb calorimeter, the value will vary with alterations in the surroundings of the bomb, and the interchange of heat between the calorimeter and its environment is practically proportional to the difference in their temperatures Consequently the water equivalent of the bomb should be determined under exactly the same conditions as will be used for the combustion of the coals All the mechanical arrangements, its position in the room, the shields, the stirrer, etc , should be decided upon before the determination of the water equivalent of the apparatus is carried out

The only reliable method of determining the water equivalent for ordinary practice, is by burning a substance of known calorific value Naphthalene, cane sugar, benzoic acid, have been widely adopted as standard substances, but it is considered that benzoic acid is the most suitable With naphthalene it is difficult to ensure complete combustion, and its calorific value is somewhat uncertain, different authorities giving from 9,628 to 9,718 calories The objection to cane sugar (3,954 calories) is that its calorific value is low, and consequently the conditions under which the test is carried out are not exactly comparable with those existing when coal is examined.

In carrying out the determination with a standard substance (benzoic acid) sufficient should be taken to produce a rise in temperature such as would be obtained with one gram of average coal , the temperature differences between the calorimeter and its environment will then approximate to those of an actual determination.

The benzoic acid is made into a briquette, and the determination carried out in exactly the same manner as that described later under the heading of method of manipulation

A second method of determining the water equivalent is to obtain the weight of the various parts of the calorimeter which are directly affected by the heat from the bomb. The water equivalent of each part can be calculated by multiplying the weight by its specific heat. The following values are required in the Mahler-Kroecker and Mahler-Cook calorimeters

SPECIFIC HEATS.

MAHLER-KROECKER & MAHLER-COOK BOMB CALORIMETERS

	Specific Heat	Part of calorimeter
Copper	0·0915	calorimeter vessel and stirrer
Lead	0·0290	washer
Platinum	0·0324	inlet tube crucible and terminal, and platinum disc
Silica	0·1977	crucible
Steel	0·1100	bomb
Mercury	0·0333	
Thermometer	0·45 calorie per cubic centimetre	

The water equivalent of the author's apparatus is 370 grams

The second bomb calorimeter used by us is that supplied by Messrs. C W Cook, Ltd ,* which differs in certain details from that of the Mahler-Kroecker bomb This particular instrument is used under conditions which are not quite so ideal as those described in the preceding pages, owing to lack of space in the particular laboratory in which the determinations have to be carried out. The instrument is not in an enclosed chamber, and the reading of the thermometer is made by means of a D×10 lens.

The method of ignition is by a small fixed open resistance and a switch The water jacket of the calorimeter is not only polished, but it is covered with thick felt which reduces the heat lost by radiation. The stirrer is maintained at 90 strokes per minute, as owing to the volume of the bomb there is a tendency for the liquid to splash if the speed is increased to that used with the Mahler-Kroecker bomb

The bomb

The construction of the Mahler-Cook bomb may be gathered from Figure 2. The water equivalent is about 650 grams as compared with that of the Mahler-Kroeker bomb of 370 grams The head differs completely from that of the Mahler-Kroecker bomb, and consists of a powerful nut of hexagon shape, having a special spigot joint (a). The joint is fitted with a lead washer and the manipulation of the head in order to obtain a perfectly gas-tight joint is simpler than that of the Mahler-Kroecker bomb. The nut has free movement on the actual head of the bomb, and the crucible and its contents are not disturbed during the manipulation In the case of the Mahler-Kroecker bomb, as the lid is being screwed into position the crucible and its contents are revolved, and this causes misfires owing to the wire for ignition and the briquette of coal becoming displaced The wear and tear on the washer is less than that in the Mahler-Kroecker bomb, where there is a rubbing action In the case of the Mahler-Cook bomb the two surfaces are brought together by simple pressure and there is actually no twisting action upon the washer In this respect the Mahler-Cook bomb has advantages over the Mahler-Kroecker bomb, and as it is one of the vital points in the manipulation of the bomb, the consideration must be taken seriously into account in deciding which of the two forms of apparatus to instal.

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*The University Works, Manchester

The means by which the oxygen is introduced into the bomb are similar to those of the Mahler-Kroecker bomb, except that the valve is guided by a hand wheel (b) three inches in diameter, and thus more perfect control is possible Leakage of the inlet valve occasionally occurs, due most frequently to the cone (c) becoming rusty owing to the action of the acid gases in the waste products. The trouble may be remedied by cleaning the cone with emery paper, or the cone may be re-ground without trouble The latter has only been necessary three times whilst 1,700 determinations have been carried out. It is not advisable to remove the spindle more frequently than is absolutely necessary, as the packing may become disturbed

Platinum wire is used and 33 per cent of the value of the wire is recovered from the waste platinum. A platinum crucible (d) is part of this instrument and the wear and tear upon it is greatly reduced by using platinum as the igniting wire. If iron wire is taken there is a tendency for the crucible to depreciate in value.

Method of manipulation of the Mahler-Kroecker apparatus

The following is a brief description of an actual determination of the calorific value of a sample of coal in the Mahler-Kroecker bomb. It will be assumed that the conditions of the calorimeter are those described earlier in this bulletin

The calorimeter vessel is charged with 2130 grams. of water, the temperature of which should be that of the chamber in which the determination will be performed The actual volume of water taken should be such that only the two terminals of the Mahler-Kroecker bomb project above the surface

One gram of coal, pulverised to pass through a 1/90 mesh is placed in the cylinder of the briquette making press, and a length of eight centimetres of iron wire weighed and arranged so that it passes into the coal to a depth of about one-eighth of an inch The press is then assembled, and the coal compressed into a small briquette It is then removed, when the iron wire should be firmly embedded in the briquette The whole is now weighed, and by deducting the weight of the iron wire, that of the coal is obtained ; for ordinary coals the weight should not exceed one gram The separate ends of the iron wire are now attached to the terminals (c) and (d) on the head of the bomb, and below the briquette is placed a silica crucible (e), so that the coal just touches the bottom of the crucible The screw of the bomb calorimeter is now covered with a thin coating of vaseline, and the lead washer in the head or lid carefully wiped to remove dust 10 c.c of distilled water are introduced into the bomb and the head of the bomb is now screwed home, by the aid of a long lever , considerable pressure must be exerted The inlet-valve (f) is attached to the oxygen cylinder, and the pin valve opened just half a turn, the outlet valve (g) being closed The oxygen is then turned on at the cylinder until the pressure in the bomb as shown on a gauge reaches 25 atmospheres It is not necessary to emphasise the fact that the oxygen should only enter the bomb calorimeter slowly When the desired pressure has been attained, the pin valve (h) is closed by simple pressure of the fingers A perfectly gas-tight joint can be obtained by this means, without undue pressure being exerted Any excess of pressure means that the surface between the valve and its seating gradually becomes distorted until finally the seating will require re-grinding, or the head may be rendered entirely useless. The attachment to the oxygen cylinder is now removed and the main valve (f) replaced The electrical terminals which pass through the lamp resistance are attached to the terminals of the head of the bomb by thin unprotected copper wire, 4 inches in length connected to insulated wire (j) The bomb is now carefully lowered in the calorimeter vessel, the stirrer introduced, the thermometer placed in its position, and the vulcanite lid replaced The stirrer (s) is now started and rated at 100 strokes per minute. The glass door of the calorimeter cupboard is closed, and the whole allowed to stand with the stirrer running for at least five minutes At the expiration of this period the actual determination may be started Readings of the thermometer are now taken to 1/1000°, at one minute intervals and are recorded as the pre-ignition readings. These readings should be taken for a period of ten minutes, but it will be found that working under the conditions described above a uniform temperature is attained in five minutes At the end of the tenth minute the electrical connection which heats the ignition-wire is made, the readings of the thermometer are continued at half-minute intervals, the eleventh, twelfth, etc. being placed on record, although the temperature may be rising very rapidly. The reading is obtained at the end of every half minute, until the maximum temperature has been recorded, when the post-ignition values are placed on record for an additional ten minutes. The actual determination is now complete except for the estimation of the sulphuric and nitric acids remaining in the bomb. The bomb is removed from the calorimeter vessel, thoroughly dried, the outlet valve opened cautiously, and the gases allowed to escape The head is then unscrewed, and the bomb and the head are washed out with distilled water into a beaker. This liquid contains the sulphuric and nitric acids produced by the oxidation of the sulphur in the coal, and the nitrogen in the coal, oxygen and air in the bomb The crucible and bomb should be carefully examined for indications of incomplete combustion. Especial attention should be paid to the ash of the coal remaining in the crucible as it is frequently in a fused condition and forms beads in which small quantities of unburnt carbon may be detected.

The liquid from the bomb is titrated with deci-normal caustic soda, using methyl-orange as the indicator, the volume of caustic soda required shows the total amount of acid present in the liquid The liquid is now made slightly acid with hydrochloric acid, and filtered to remove any particles of platinum or iron wire and ash The filtrate is then heated to boiling, and a slight excess of a boiling solution of barium-chloride added. The liquid is allowed to digest and then placed on one side to allow the barium sulphate to separate The barium sulphate is then filtered off, washed thoroughly, dried and ignited The weight of barium sulphate multiplied by 0·4206 is the amount of sulphuric acid present in the liquid The weight of acid is calculated to the equivalent volume of deci-normal caustic soda, and the volume thus obtained deducted from the total obtained in the titration of the liquid. The excess is the volume of deci-normal caustic soda required to neutralise the nitric acid in the liquid

Where the percentage of sulphur in the coal is known, it is quite accurate to calculate the amount of sulphur in the weight of coal taken for the calorific determination, and from this the weight of sulphuric acid which would be formed when it is oxidised. The volume of deci-normal caustic soda equivalent to this acid is then calculated and deducted from the volume of caustic soda required in the titration of the liquid from the bomb The difference is the volume required to neutralise the nitric acid produced in the determination.

Frequent observations have been made as to the amount of sulphur remaining in the ash, and as a general rule where the percentage of ash is not greater than 10, the error introduced by this procedure is comparatively small.

It is clear that the above forms a rapid method for the estimation of sulphur in coal, and the time required for the determination is considerably reduced as compared with Eschka's method.

The following is a typical example of a determination of the calorific value in the Mahler-Kroecker bomb with the method of calculation of the corrections —

Date · 6/6/21

Sample No . 523/F

Readings

Time	Temperature °C	
11·41	14·960	$\beta = +0{\cdot}001$
42	14·960	
43	14·960	
44	14·955	
45	14·955	
46	14·955	
	ignited	
46½	15·200	n = 3
47	16·900	
47½	17·620	
48	17·780	
48½	17·820	
49	17·825	
	maximum	
50	17·820	$a = +0{\cdot}013$
51	17·805	
52	17·792	
53	17·780	
54	17·765	
55	17·755	
56	17·755	

Coal .. .. = 1·0000 gm

Water in bomb = 10 gms

Water equivalent (Bomb 370 gms plus Water 2130 gms) . .. = 2500 gms.

Total water equivalent (W) .. = 2510 gm

Calorific Value

$= \{(R \times W) - (A + I)\}\ 1{\cdot}8$ B Th Us.

$= \{(2{\cdot}903 \times 2510) - (39{\cdot}36 + 20{\cdot}93)\}\ 1{\cdot}8$

$= (7286 - 60{\cdot}3)\ 1{\cdot}8$

= 13,006 B Th.Us. per lb

CORRECTIONS

Radiation Correction

$$(n-1)\,a + \left(\frac{a+\beta}{2}\right)$$

$$= 2 \times 0{\cdot}013 + \frac{0{\cdot}014}{2}$$

$$= 0{\cdot}026 + 0{\cdot}007 = 0{\cdot}033^{\circ}\mathrm{C}.$$

True Rise of Temperature (R)

	°C
Observed final temperature ..	= 17·825
Observed initial ,, .	= 14·955
,, temperature rise .	= 2·870
Radiation correction . ..	= 0·033
True rise (R)	= 2·903

Correction for Iron Wire (I)

Length of Wire . . = 8 cms

,, ,, ,, unburned = nil

,, ,, ,, burned = 8 cms

Weight of Wire ,, . = 0·0246 gm.

Heat due to wire (I) = 1600 × 0·0246
= 39·35 calories

Acid Correction (A)

Titration = $4{\cdot}9$ c c $\frac{N}{10}$ NaOH solution
= 0·02839 gm H_2SO_4

H_2SO_4 determined gravimetrically = 0·0273 gm

Remainder = HNO_3
0·00109 gms H_2SO_4

$$= \frac{63}{49} \times 0{\cdot}00109 \text{ gm } HNO_3$$

$$= 0{\cdot}001402 \text{ gms } HNO_3$$

Heat due to S. = 0·0273 × 755
= 20·61

,, ,, ,, N. = 0·001402 × 226·6 = 0·32

Acid Correction (A) .. = 20·93 cals

Note on Corrections to be applied

(1) *Radiation correction* This is found from the following formula :— $(n-1)\ a + \frac{a+\beta}{2}$

where n = number of minutes during which the temperature rises after firing

a = average change in temperature per minute after the maximum has been attained
β = average change in temperature before firing
} These have positive values for a temperature fall.

(2) *True rise of temperature* is found by adding the radiation correction to the observed rise of temperature.

(3) *Correction for iron wire* The iron wire used to ignite the coal in the bomb is taken as having a calorific value of 1600 calories per gram This value, multiplied by the weight in grams of iron wire which has actually burned, gives the correction which has to be deducted from the amount of heat produced

(4) *Acid correction.* The acidity is calculated from the amount of caustic soda used, as sulphuric acid, but actually consists of nitric acid as well. The amount of sulphuric acid is determined and deducted from the acidity already found and the difference is calculated as nitric acid by multiplying by

$$\frac{\text{equivalent weight of nitric acid}}{\text{,, \quad ,, \quad ,, \quad sulphuric acid}} = \frac{63}{49}$$

When 1 gram of sulphur burns to sulphuric acid in the bomb it liberates 4,450 calories. In ordinary combustion the sulphur burns to sulphur dioxide, the heat of formation of which is only 2,250 calories Hence the deduction to be made from the calorimeter determination is $4450 - 2250 = 2200$ calories per gram of sulphur or $\frac{2200 \times 32}{98}$

755 calories per gram of sulphuric acid

Similarly with nitrogen, 1020 calories are produced by the combustion of one gram of nitrogen or $\frac{1020 \times 14}{63} =$ 226·6 calories per gram. of nitric acid, and since this nitrogen is not burned under ordinary conditions of combustion, the whole of the heat produced in the bomb by the oxidation of nitrogen has to be deducted

(5) *Calculation of calorific value.* The total water equivalent of the bomb and calorimeter (W), multiplied by the true rise in temperature (R) is the total amount of heat given out by the combustion in the bomb. From this must be deducted the corrections for the iron wire burned and the acids formed, as explained above. This yields the calorific value in calories This value must be multiplied by 1 8 to obtain B Th.Us per pound.

The authors wish to express their thanks to Mr A. Mc.Culloch, A I C and Mr. C G Wood, M Sc. (Tech.), A I.C. for help in the preparation of certain parts of this bulletin.

72

A CONTRIBUTION TO THE STUDY OF THE STONE DUSTING OF MINES

(PART II)

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With a Section by
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922

BULLETIN XI

PREFATORY NOTE

This bulletin was prepared in order that members of the Research Association should have at their disposal a brief, but comprehensive, account of the principles underlying the problem of the stone dusting of mines.

It is thought that the information may be of interest to others who have to deal with this subject, which affects not only the safety of mines, but the health of the miners.

R. A. BURROWS,
President of the Lancashire and Cheshire Coal Research Association

Atherton Collieries,
Atherton

A CONTRIBUTION TO THE STUDY OF THE

STONE DUSTING OF MINES

(PART II)

This bulletin has been primarily prepared as a précis of the considerations which have given rise to Government Regulations governing the Stone-dusting of Mines (No. 4, General Regulations made under the Coal Mines Act, 1911, and dated 30th July, 1920. S R & O, 1920, No. 1423, Part I, Section 62, and S R. & O, 1921, Nos 200 and 201). It embraces work carried out under the auspices of the Lancashire & Cheshire Coal Research Association with a view to determining the suitability of shales for stone-dusting, and methods of economising the time for grinding such shales to a requisite fineness of division.

The concluding paragraphs of the Final Report of the Royal Commission on Accidents in Mines (1886) states that :

" The observations recently made in Germany in some preliminary experiments, that a thin layer of fine angular sand strewn over mine dust appeared to have the effect of preventing the communication of flame from a blown-out shot to all but the most inflammable dusts is worthy of passing notice."

Many investigators, amongst whom may be mentioned Dr W N and J B. Atkinson and Professor W Galloway, had already recognised the danger arising from coal dust, but it remained for the Mining Association of Great Britain, at the instigation of The Royal Commission on Mines in 1908, to demonstrate definitely that,

(1) Coal dust was explosive without the presence of inflammable gas (May 30th, 1908).
(2) Dustless zones were ineffectual (June 15th, 1908).
(3) Stone dust would extinguish an explosive flame

Since this date many scientific and practical men have studied, in this and other countries, the factors which contribute towards the liability of coal dust to form explosive mixtures when suspended in air, and the following have been more or less systematically examined ·

(*a*) Fineness of division of coal dust (*b*) Volatile content of coal dust. (*b2*) Presence of carbonates in coal dust and mine dust. (*c*) Moisture content of coal dust. (*d*) Ash content of coal dust (*e*) Friability of coal (*f*) Quantity of coal dust. (*g*) Composition of the atmosphere in the mine (*h*) Air velocity of the pioneering wave preceding an initial explosion. (*i*) Composition of inert material. (*j*) Fineness of division of inert material.

(*a*) *Fineness of division of coal dust.*
The fineness of division of the coal dust has a direct bearing upon its liability to form explosive mixtures. The more finely divided the dust the greater is the tendency of the resulting suspension in air to explode

Bedson (Trans Inst Min E, 1909-10, Vol 39, p. 719) gives the following table

Fineness of Division of Coal Dust		Current required to inflame Dust and Air.
Over 1/120 mesh sieve	... ...	12·0 amps
1/120—1/150 mesh sieve	.	10·5 „
1/150—1/200 mesh sieve	... ...	10·25 „
Through 1/200 mesh sieve	.. .	9·75 „

Cadman (*ibid.,* p. 93) quotes the following figures showing the relationship existing between the degree of fineness and the temperature of ignition of suspensions of coal dust in air ·

Fineness of Dust	Ignition Temperature.	Percentage of Ash in Sample.
1/100 to 1/150 mesh sieve	2463° F. (1350° C.)	1·50
1/150 to 1/180 mesh sieve	1652° F. (900° C)	1·57
1/180 to 1/220 mesh sieve	1562° F. (860° C)	1·80
Through 1/220 mesh sieve	1362° F. (850° C.)	1·98

Halbaum (Trans.Inst.Min.E., 1909-10, Vol. 39, p. 728) points out the effect of fineness of division of coal dust, by a consideration of the effect of the pulverisation of one piece of coal upon the surface area of the coal exposed and consequently upon the exudation of occluded gas, from the "pores of outlet or exudation," as distinct from the pores within the solid piece of coal—by pores meaning the molecular interspace in the coal. Equally important is the production of absorbent surface and consequent "soaking up, so to speak," of oxygen, and the production of heat through such rapid soaking up of oxygen.

Halbaum expresses the opinion that, moderately judged, each impalpable particle of coal dust has a diameter less than 1/60,000 inch, and states:

"If the impalpable particle of coal dust be 1/nth of an inch in diameter, and n=60,000, we have the information that the heating, exuding or absorbing surface presented by 10 lbs of impalpable coal dust is at least n=60,000 sq yds This surface is equal to the surface of a long-wall face 6 ft, high and 17 miles long"

In a discussion on this paper it was suggested that dust particles were never finer than 1/10,000 inch diameter, but even if this be assumed 10 lbs. of coal dust have a surface of 10,000 sq. yds.

(b) *Volatile content of coal dust.*

The proportion of volatile matter evolved when a coal is heated plays an important part in its sensitiveness to inflammation. Bedson (loc. cit.) quotes the following figures:

Artificially Pulverised Dusts

Coal	Moisture	Vol Matter	Fixed Carbon	Ash	Ratio Fixed Carbon to Vol Matter	Ratio Fixed Carbon & Ash to Vol. Matter	Relative Pressure of Explosion
1.	1·52	34·01	58·55	0·94	1·50	1·51	5
2.	6·08	38·22	52·85	2·85	1·38	1·46	5
3	8·58	31·89	57·78	1·81	1·81	1·86	2

Naturally Pulverised Dusts

Coal	Moisture	Vol Matter	Fixed Carbon	Ash	Ratio Fixed Carbon to Vol Matter	Ratio Fixed Carbon & Ash to Vol. Matter	Relative Pressure of Explosion
4.	1·07	27·49	63·72	7·72	2·32	2·59	4
5	5·20	29·05	42·22	23·60	1·45	2·27	1·5
6.	5·01	28·38	37·08	29·60	1·30	2·35	1·5

Substances which yielded a high percentage of inflammable compounds on heating were compared with coal for the same degree of fineness (1/200 mesh).

	Current required to inflame	Vol Matter by Prox Assay Test
Starch	8 5 amps	97·9 per cent.
Sugar	8·5 „	91·4 „
Flour	9 9 „	88 7 „
Coal	11 5 „	28·55 „

The sensitiveness to inflammation shows a systematic gradation from brown coal to anthracite, varying broadly according to the percentage of the volatile matter present. In this connection the influence of the volatile matter is emphasised to a great degree by the following figures which correlate the pyridine extract, residue, and the original coal—"the extract comports itself like a brown coal and the residue behaves somewhat like anthracite."

	Ratio—Fixed Carbon to Vol Matter (calculated on dry, ash-free samples)	Current in Amps
Pyridine extract of coal	0·66	10·5
Residue of coal	2·00	15·0
Original coal	1 86	11·5

This brief outline of the probable influence of the volatile matter may be concluded by the statement emanating from the Lieven Testing Station, J Taffanel (Trans Inst.Min E., 1910-11, Vol 40, p. 365), expressing the opinion that coal having a lower percentage of volatile matter than 11 per cent. may be considered to be relatively safe.

(b2) *Presence of Carbonates in coal dust and mine dust.* It has been shown that many coals may contain a high percentage of carbonates, and in "The Determination of the Carbon Dioxide in Coal" (Sinnatt and Harrison, Bulletin 7, Lanc. Ches Coal Res Ass) results are given showing that abnormal coals may evolve 6 to 18 per cent of their weight on treatment with acids During the ignition for the volatile matter test, the carbonates present undergo decomposition, and the carbon dioxide is evolved and recorded as volatile matter This is particularly of interest in view of the S R O, 1921, No 200, in which a procedure is prescribed for the determination of the amount of combustible matter in samples of mine dust which contain carbonates, such regulations being available to meet cases in which carbonates such as limestone are employed as an inert material.

It has been suggested that such dusts by virtue of the carbonic acid gas that they liberate when strongly heated should be particularly effective in preventing the ignition of coal dust. Large scale experiments carried out by the Explosions in Mines Committee (6th Report, Cd 7368), page 12, supplemented by laboratory experiments do not, however, support this suggestion, and it is stated in this report that, "it is true that a carbonate of which the temperature of decomposition is very low—such as sodium bicarbonate—is more effective than other incombustible dusts, whether on account of the carbonic acid gas evolved, or by reason of the steam simultaneously liberated it is difficult to decide But with the majority of the carbonates the decomposition temperature is too high, and the rate of evolution of carbon dioxide consequently too slow for them to perform any function other than that of 'inert' materials"

(c) *Moisture content of coal dust*

The moisture present in coal has a retarding action upon the liability of dusts to explode, and moistening the coal may be considered in the same light as mixing it with stone dust Experiments carried out in America (Trans Inst Min E., 1910-11, Vol. 40, p. 368) have proved that the presence of 30 per cent. of water in any bituminous coal dust renders the dust practically non-explosive Austrian experiments (Colliery Guardian, 1909, Vol. 98, page 635) quote the following figures .

Percentage of Moisture in Coal Dust.	Length of Flame resulting from Explosion of Suspension of Coal Dust in Air.
0·36 to 1·06	220 yds.
4·05 to 6·0	64 yds.
7·55	No explosion took place
10·17	No explosion took place

The conclusions with regard to the wetting of coal dust arrived at by the Explosions in Mines Committee (loc. cit, p. 15) are stated as follows .

"Our experiments have shown that the wetting of coal dust in a gallery can be effected best by a fine mist of water which sinks into and is absorbed by the dust. Pure coal dust (containing 5 per cent of ash) requires to be so wetted as to contain 10 per cent. of water throughout to prevent propagation of flame when 24 ozs of powder were fired into it. With coal dust wetted *in situ* it required an equal weight of water to be used in the form of fine mist to secure that the large flames produced (1) by the cannon and 5 lbs of dry coal dust and (2) by the explosion of coal gas and air through 150 ft. of the 3 ft. gallery, should not be propagated through the wet coal dust."

And further, "the maintenance of at least 30 per cent. of water in a state of intimate mixture with the dust throughout the roads would prove effective in greatly minimising, if not preventing, explosions of coal dust."

At the same time it should be pointed out that it is extremely difficult to so apply water to coal dust that the whole of the coal dust is thoroughly wet. This particularly applies in dealing with fusain, which has been shown to constitute 20-50 per cent. of mine dusts.

(d) Ash contents of coal dust.
The ash present in coal has a retarding influence upon the liability of the dust to explode Harger (Trans.Inst Min.E, 1911-12, Vol. 43, p. 132) attempts to co-relate the percentage of ash with the liability of the dust to explode with the following results :

	Current required to ignite constant.	
Ash in screen dust	10·4	No ignition
Ash in dust from intake haulage road (1)	33·9	
Ash in dust from intake haulage road (2)	19·5	
Ash in dust from coal prepared in laboratory	1·3	Ignition

According to Sinnatt (Trans.Inst.Min.E., 1921, Vol. 62, pp. 156-171 and 172-179), screen dust and mine dust may contain from 20 to 50 per cent. of fusain. Consequently the results obtained by Harger may possibly [illegible] explained as due to the non-explosive properties of fusain.

In the experiments at the Austrian Experimental Station it has been shown that with dust containing 14 per cent. of ash explosions were easily produced, but as the ash content increased the violence of the explosion diminished, and when 48 per cent was reached explosions were no longer produced The various percentages of inert matter necessary to prevent a bituminous dust from forming explosive mixtures when suspended in air have been determined, and vary with the nature of the inert material employed. The 50 per cent. ash content stipulated in the Stone Dust Regulations has been chosen as a safety limit for all bituminous coal dusts, although it is stated (loc cit, p. 15) "that the maintenance throughout the roads of such a proportion of incombustible dust in a state of fine division as would make a mixture yielding on incineration at least 50 per cent. of ash, would prove effective in very greatly minimising if not preventing explosions of coal dust." (At the same time it should be pointed out that according to the Austrian experiments the limit of danger was not passed until the percentage of stone dust reached 57 per cent.)

(*e*) *Friability of coal.*

It is generally recognised that coals vary in their degree of friability, and if a measure of the relative friabilities of coals could be obtained a clear impression of the liability of such coals to yield dust and consequently explosive mixtures could be gathered.

Dr. R. V. Wheeler, in evidence before the Departmental Committee on Spontaneous Combustion of Coal in Mines (Minutes of Evidence, 23rd to 26th Days, Question No. 13,013), discussing the effect of friability on spontaneous combustion stated:

"The relative friabilities were determined by putting a given weight of coal, all in the form of nuts of about 2 inches cube, into a ball mill, with a certain weight of steel balls and grinding for a given period and finding how much dust was formed. It was a rough method, but it gave us relative figures for friabilities"

Experiments by one of us indicate that the method of determining the relative friability by grinding a certain weight of coal under absolutely standard conditions and comparing the percentages passing through a 200's mesh sieve with those obtained from other coals are not altogether to be depended upon

(f) Quantity of coal dust.

Experiments were made at The Lievin Testing Station to determine the quantity of coal dust per unit of air space necessary to cause a dust explosion. The gallery in use was 6 ft high, 5 ft wide, and some 500-600 yds long, and the prepared coal dust, containing 4 per cent of ash and 30 per cent. of volatile matter was reduced so that the whole would pass through a 200s. mesh sieve. A charge of gelatine-dynamite was fired from a cannon to cause the initial explosion in the gallery, and the experiments were carried out in still air It was found that 3 ozs of fine coal dust per cubic yard of space in the gallery was sufficient to cause a dust explosion in the entire absence of fire damp.

Other investigators have shown that the quantity of coal dust necessary to cause an explosion when suspended in air is comparatively small, and it would appear, consequently, that endeavouring to keep mine roadways clear of coal dust is useless as a sole preventative measure. At the same time, the employment of dust proof tubs and the systematic cleaning of roadways is to be advocated in conjunction with efficient stone-dusting in view of the relative quantities of coal dust and stone dust present in any one place in a roadway

(g) Composition of the atmosphere in the mine.

According to J Harger (Trans.Inst.Min.E, 1911-12, Vol. 43, p 131) the composition of the atmosphere affects the liability of dusts to form explosive mixtures An increase in the percentage of oxygen present in the air accelerated such liability and the converse is also true. The following table shows the results obtained by Harger .

Oxygen. Per cent	Nitrogen. Per cent	Remarks
16	84	No ignition
17	83	„
18	82	„
18½	81⅓	Partial ignition
19	81	Just full ignition

Following Harger's experiments the Explosions in Mines Committee (loc. cit.) determined the reduction of oxygen in air necessary to render methane and coal dust non-explosive. "With regard to methane the results were as follows :

Per cent. Oxygen Content of Atmosphere	Lower Limit of Inflammability, per cent. of Methane.	Upper Limit of Inflammability, per cent. of Methane
20·9	5·6	14·8
19·4	5·8	12·9
17·0	5·8	10·5
15·8	5·9	8·9
14·8	6·1	8·3
13·8	6·4	7·3
13·5	6·5	6·8
13·2 and under	No mixture is capable of propagating flame	

Above the limit of 13·25 per cent. of oxygen, an explosion of methane in such air is still possible, provided the right quantity of methane is present to produce it. But when the proportion of oxygen has been reduced to 17 per cent., a reduction that is not, we believe, desirable in air which men and animals have to work in, any admixture of methane between the limits of 5·8 per cent and 10·5 per cent is still explosive"

With regard to coal dust, carrying out a series of experiments in a spherical bomb, "it was found that explosions which developed pressure amounting to 90 lbs per sq. inch were readily obtained from Silkstone coal dust in air containing 19 per cent., 18 per cent., and 17·5 per cent of oxygen No ignition could be obtained under the conditions of the experiments when the air contained only 17·1 of oxygen. When, however, the atmosphere also contained 2 per cent. of methane, the oxygen had to be reduced to 16 per cent. before it became impossible to ignite the mixture"

(*h*) *Air velocity of pioneering wave preceding an initial explosion.*

A distinct factor in the problem is the degree of disturbance caused in the coal dust and stone dust by the current of air produced by the explosion passing through the galleries (pioneering wave), and Garforth (Trans Inst. Min E, 1912-13, Vol. 45, p. 572) stated that a velocity of less than 1,500 feet per minute did not disturb ordinary dry coal dust, but at a greater rate the coal dust was raised and carried away as a cloud Stone dust was not disturbed until a velocity of 2,600 feet per minute (29 5 miles per hour) has been reached, when it was carried away by the air current as a cloud. In the Altoft's experimental gallery one of the lowest velocities recorded as the speed at which an explosion travelled was 120 miles per hour, or 4 times faster than the air current which would raise both coal dust and stone dust as a cloud. The rate of travel of the more violent explosions was 300 miles per hour, and in one particular experiment 1,300 miles per hour was reached.

From the above it would appear that the whole of the stone dust present would be raised as a cloud by the pre-wave of the explosion and the explosion would be stopped or considerably modified provided the percentage of stone dust was not less than that required by the Government Regulations, even if subsequent layers of coal dust overlay to some extent the layers of stone dust already laid down

(i) Composition of inert material.

In view of the fact that dusts of widely different composition are being offered as suitable substitutes for stone dust, e g, Chance's mud, waste cement, etc, the investigation carried out by A S Blatchford on "The Influence of Incombustible Substances on Coal Dust Explosions" (Trans.Inst Min.E, Vol. 51, 1915-16, p. 369) is of interest. Coal dusts ground so that the whole passed through a 100's mesh sieve were employed and mixed with various agents, pulverised to as fine a state of division as possible, as quenching materials or coal dust dilutents.

The following table shows the least percentage of quenching material in the mixtures which prevented an explosion, in a specially designed apparatus.

Coal.	A	B	C	D
Boiler Ashes	57	50	47	58—60
Quicklime	50	45	42—44	55
Ground Shale	43	37	35	46
Chance's Mud	38—40	30—33	29—30	39—40
Gypsum	33—35	26—28	26	35
Magnesia	28—30	28	25—26	32—33
Anhydrous sodium carbonate	12—13	10+	12	15
Soda crystals ($5H_2O$)	10	10−	9+	11
Soda bicarbonate	9—10	7	7	8−
Glauber salts ($6H_2O$)	8	8	7−	8−

Blatchford recognises that the evolution of carbon dioxide from a quenching material has but a small influence upon the explosive character of the mixture, and concludes that the difference in behaviour between these compounds is most satisfactorily explained on the hypothesis that the specific heat of the quenching material is the imporant factor in its efficiency

(j) *Fineness of division of inert material.*

From a consideration of the effect of the fineness of division of the coal dust upon its liability to form an explosive mixture when suspended in air (p. 4), it will be readily recognised that the finer the division of the material the more efficient is such material as a coal dust dilutent Probably such inert material is effective by virtue of the cooling effect exerted by each particle, and is directly dependent upon the surface area of the inert material exposed.

The Explosions in Mines Committee (loc. cit) give the following results illustrative of the point

"We have made comparative experiments with the following materials of different degrees of fineness, using coal dust of the same degree of fineness in each experiment (namely, such that the whole passed through a safety-lamp gauze, and about 70 per cent. through a 200×200 sieve):

Material.	Percentage by Weight that passed through. 28 x 28 Sieve.	200 x 200 Sieve.
(1) Sand	99	4
(2) Altoft's shale	65	18
(3) Flue dust	90	31
(4) Dolomite dust ("fine")	68	42
(5) Altoft's shale (reground)	98	55
(6) Dolomite dust ("superfine")	96	66

The materials numbered 5 and 6 on the list were effective in preventing the propagation of the flame from a cannon shot when mixed with the coal dust in the proportion of 1 : 1. Of either the materials numbered (3) and (4) 1½ : ½ of coal dust was required · of Altoft's shale (2) 2 : 1 of coal dust was necessary, whilst three parts of sand to one of coal dust was not found to be sufficient."

EXAMINATION OF SHALES TO DETERMINE THEIR SUITABILITY FOR STONE DUSTING

The question of the suitability of a shale for conversion into stone dust is decided mainly by the quantity of organic matter present in the shale and by the physiological effect the shale may have upon the workers in the pit.

Methods for the chemical analysis of shale are described below, namely, (1) Total analysis and (2) rational analysis.

No accurate method of determining quantitatively the free quartz in shale is available, and reference is made to the microscopical examination on page 20.

(*a*) *Total Analysis.*

It is not proposed to describe in detail the chemical analysis of shale as it can be found in most text books on chemical analysis (e.g., Mellor, " Methods of Chemical Analysis ") Briefly shale is treated in the following manner :

The finely pulverised shale is mixed with a fusion mixture of sodium and potassium carbonates, and ignited in a platinum crucible When the ignition is complete the fused mass is washed from the crucible and treated with hydrochloric acid The liquid is then evaporated to dryness, and the residue finally heated to 110° C. for one hour The mass so obtained is treated with dilute hydrochloric acid, and the silica which is thus separated is removed by filtration. After washing thoroughly the silica is treated in the usual manner, and the amount determined. The filtrate is diluted to a known volume, and the iron and aluminium, manganese calcium, and magnesium determined in an aliquot portion. The sulphur trioxide is determined in a separate portion. If it is necessary to determine the sodium and potassium a fresh sample of the shale is fused with calcium carbonate or pure lime (Laurence Smith's method).

Moisture.

One gram of the finely pulverised shale is spread finely over a watch glass or shallow flat-bottomed dish, and heated in an air oven for one hour at 105° C. It is covered and transferred to a desiccator and allowed to cool. It is then re-weighed, and the loss represents the moisture in the shale

Loss on Ignition.

About one gram of finely pulverised shale is weighed into a silica dish and heated in a muffle at about 800° C. in such a manner that it does not come into contact with the products of combustion of the gas. It is allowed to remain in the muffle for about an hour It is then removed to a desiccator, allowed to cool, and re-weighed. The loss in weight is hygroscopic water, combined water, carbon dioxide, and organic matter There may be a slight gain due to the oxidation of any sulphur which may be present.

Carbon Dioxide.

The percentage of carbon dioxide in shales is generally relatively small, but as it is a factor which influences the loss on ignition the determination is of some value. The method described in the Determination of the Carbon Dioxide in Coal (Sinnatt and Harrison, Bulletin 7, Lanc. Ches. Coal Res Assoc) is considered to be the most convenient one for the purpose. Apparatus of the type of Schrotter yields inaccurate results, as the amount of carbon dioxide seldom exceeds 5 per cent On the other hand, certain dusts offered as substitutes for shale dust contain about 40 per cent. of carbon dioxide, and in such a case apparatus of the Schrotter type may be employed.

Rational Analysis.

(Extract from Technical Methods of Chemical Analysis, G. Lunge and C. A. Keane, Vol 1, Part 2, p. 587.)

" About 5 grams of shale, dried at 120° C., are covered with 50 c c. of water in a platinum or porcelain dish of about 250 c.c. capacity, and the shale thoroughly disseminated by stirring with a glass rod or thick platinum wire. 50 c.c. of concentrated sulphuric acid are then added, and the whole again mixed. The dish is then covered with a clock glass, heated over the free flame until its contents boil, and the heating continued until the sulphuric acid fumes strongly. The contents of the dish are then allowed to cool, diluted with water, and stirred after a short time the supernatant liquid becomes clear enough to be filtered off. The residue is moistened with hydrochloric acid, water added, and after stirring, the dish placed on the water bath and warmed for about fifteen minutes the supernatant liquid is then filtered off, and any solid matter which may have passed on to the filter, washed back into the dish. This treatment is continued so long as the residue colours the hydrochloric acid poured on to it (i.e., until the iron has been extracted). The residue is then transferred to the filter, thoroughly washed with hot water, then washed back into the dish, and the contained liquid diluted to 250 c.c. Crystallised sodium carbonate is then added in the proportion of 10 grams per 100 c.c. of liquid, the dish warmed on the water bath from one to two minutes, and then one gram of sodium hydroxide added for every 100 c.c. of liquid. After one or two minutes the liquid begins to clear, whereupon the dish is taken from the water bath, and the supernatant clear liquids decanted through a filter. This treatment with alkali solution must be repeated several times to make certain that the silica liberated by the acid treatment is completely dissolved. Finally the residue still left is transferred to the filter and thoroughly washed with water containing alcohol, or with dilute ammonia.

The ignited and weighed residue represents the amount of quartz and felspar present. To estimate each of these constituents separately, the residue must be treated with hydrochloric acid and with ammonia fluoride, and the alumina in the decomposed mass estimated. The amount of alumina found multiplied by 5.41 gives the amount of felspar present. The difference between this and the total residue corresponds to the amount of quartz present, provided the residue contains no mica or similar mineral detritus."

The following are some typical analyses of shales being used at present for conversion into stone dust. The shales have been analysed and also examined microscopically: they are considered to be typical examples of shale free from relatively large crytals of quartz and having a suitable composition for stone dusting. At the present stage of our knowledge they may be considered as free from any deleterious effect upon the health of any human being when inhaled.

Shale No. 1.

	Per cent Composition
Silica	60·05
Ferric oxide	5·66
Alumina	20·65
Calcium oxide	3·13
Magnesium oxide	1·89
Sulphur trioxide	trace
Carbon dioxide	,,
Water	0·99
Organic matter and combined water	7·00
Alkalis and loss	0·63
	100·00

Shale No 2.

Silica	61·13
Ferric oxide	3·84
Alumina	25·15
Calcium oxide	nil.
Magnesium oxide	1·49
Sulphur trioxide	trace
Carbon dioxide	,,
Water	1·35
Organic matter and combined water	6·12
Alkalis and loss	0·92
	100·00

Shale No. 3.

Silica	55·41
Ferric oxide	2·96
Alumina	27·11

	Per cent. Composition
Calcium oxide	0·60
Magnesium oxide	1·65
Sulphur trioxide	0·26
Water	2·70
Organic matter and combined water	7·36
Alkalis, etc., and loss	1·95
	100·00

Shale No. 4

Silica	56·91
Ferric oxide	2·80
Alumina	26·35
Calcium oxide	0·42
Magnesium oxide	1·17
Sulphur trioxide	0·69
Water	2·04
Organic matter and combined water	6·23
Alkalis, etc., and loss	3·39
	100·00

Stone Dust in use at Bentley Colliery (Robert Clive in "Stone dusting at Bentley Collieries," Trans Inst Min E., 1914, Vol 47, p. 53)

	Per cent Composition	
Silica	58·0	
Ferric oxide	7·0	
Alumina	16·0	
Magnesium oxide	2·0	
Carbon dioxide	1·5	Vol matter = 12·5 silica non-crystalline as hydrated silica.
Water	10·9	
Combustible	0·1	
Undetermined	4·5	
	100·0	

Stone Dust used in American Coal Dust Experiments (G. S. Rice, Trans Inst Min.E., 1914-15, Vol 49, p. 721. Analyst, A. C. Fieldner).

	Per cent. Composition	
Silica	50·37	
Alumina	22·43	
Ferric oxide	12·01	
Calcium oxide	1·90	
Magnesium oxide	2·06	
Sulphur	0·03	
Carbon dioxide	0·82	Loss on ignition.
Organic carbon	0·39	
Organic hydrogen	0·27	
Water	1·78	
Water of composition	5·64	
Alkalis by difference	2·30	
	100·00	

Altoft's Colliery Pit Shale (5th Report Explosions in Mines Committee).

	Per cent. Composition
Silica	51·92
Titanium oxide	0·87
Alumina	20·08
Ferric oxide	6·40
Manganese oxide	0·05
Calcium oxide	0·57
Magnesium oxide	1·56
Potash	2·72
Soda	0·86
Sulphur trioxide	0·32
Carbon dioxide	2·44
Carbonaceous matter	4·42
Combustible matter	—
Water	7·75

In the first report of the Explosions in Mines Committee (Cd. 6307) will be found an appendix by James M. Beattie, M.A., in which a study has been made of the effects of the inhalation of certain dusts upon the lungs of guinea-pigs, and from a microscopic study of the lung tissue the following conclusions are drawn .

(1) "That the effects produced in the lungs of guinea-pigs which have been exposed to the inhalation of dust correspond with those produced in man.

(2) That the effects produced vary with the time of exposure, and particularly with the quantity and quality of the dust which is inhaled

That the inhalation of such stone dusts as are rich in silica seems particularly injurious "

The opinion which is generally held with regard to the effect of stone dust upon the fibrous tissue of the lung is that this effect depends upon the nature of the silica present in the shale. Free silica or quartz on pulverisation splits up into acicular (sharp edged) particles, whereas the second type of silica which is present in shales is present in a colloidal form which is so dispersed that it cannot be identified in the matrix of the shale.

The shales which contain on pulverisation angular particles are those which are detrimental and are responsible for the irritation and injurious effects upon the lungs

It is only by a microscopical examination of the shales that it is possible to determine the condition in which the silica in the shale is present.

Microscopical Examination of Shales, by J R. Lomax.

The coal-measure shales are derived from sediment which has been laid down in water of moderate depth. They may be divided into two classes :

I. Laminated shales which show a tendency to split into slabs parallel to the bedding plane. This may be due to the mechanical rearrangement of the particles forming the rock, or the production of secondary micaceous matter which would facilitate the splitting

II. Mudstones which are simply clays which have been hardened by drying and compression and which show no fissile structure.

The particles of the two classes are essentially the same, the only difference being in the state of division of the material which often renders their separation and determination a matter of some difficulty.

There is no doubt, as will be seen from the chemical analyses which are given, that silica is the chief constituent of all shales and mudstones. Felspar is frequently present, but is often replaced by decomposition products. Micas, both muscovite and biotite, are present as primary constituents, but a large proportion of the muscovite is of secondary origin. Other minerals such as limonite, pyrites, calcite, etc., may be present, but they are all of secondary origin. Carbonaceous matter is often present in the form of fragmentary plant impressions.

For our purpose the mineralogical constituents of a shale may be divided into:

(*a*) Silica

(*b*) Alumina.

Silica is present in most shales in two forms:

I. As "free silica" or quartz grains.

II. In a colloidal form, being dispersed throughout the aluminous matter, forming a heterogeneous mass in which individual particles cannot be identified.

Petrographic examination of the shales is strongly recommended as the most satisfactory method by which it is possible to determine the quantity of "free silica" present. Under polarised light quartz grains are clearly visible, whilst silica in a colloidal form, which is really the clay base, polarises only slightly in a faint speckly manner.

The microscopical examination of the dusts made from various shales shows that if the shale contains a fairly high content of quartz grains, the dust is of an angular or acicular character. But if the constituents of the shale are of a finely divided character the dust is of a flaky nature, which is what is required for effective stone-dusting.

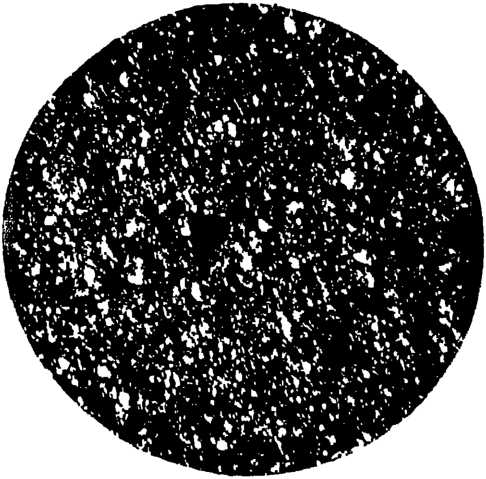
The six illustrations which are given are as follows:

1. Inferior shale showing numerous quartz grains embedded in a fine matrix. The triangular crystal in the centre is pyrites. (Not suitable.)
2. Mudstone showing the finely divided character of the constituents. (Suitable for stone dust.)
3. Inferior shale from the Middle coal-measures of Lancashire showing numerous small quartz grains. (Not suitable.)

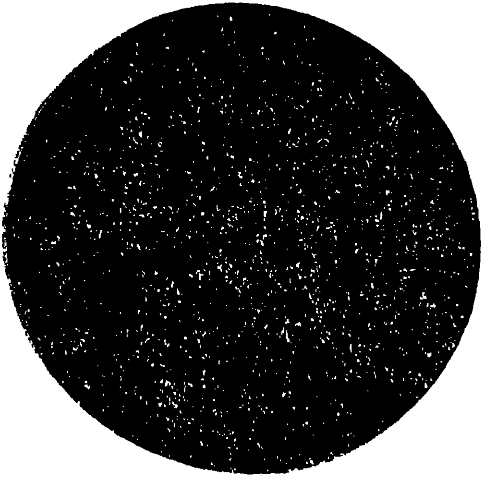
PHOTOMICROGRAPHS OF SHALES AND DUSTS

(Polarised Light)

1



2



(1) INFERIOR SHALE

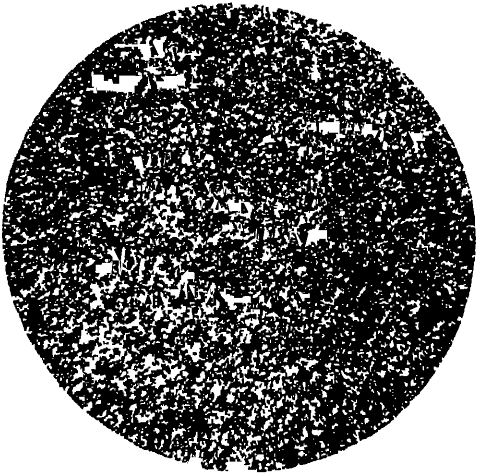
(2) MUDSTONE

(Mag. 40 Diam.)

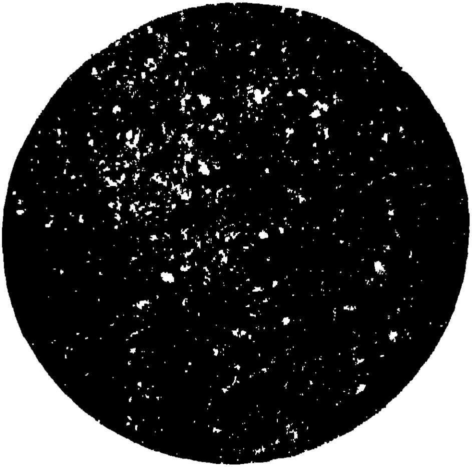
PHOTOMICROGRAPHS OF SHALES AND DUSTS

(Polarised Light)

3



4



(3) INFERIOR SHALE

(4) DUST FROM INFERIOR SHALE

Photomicrographs of Shales and Dusts

(Polarised Light)

5

6

(5) Shale Suitable for Stone Dust
(6) Dust prepared from above Shale

(Mag. 40 Diam.)

4 Dust made from No 3 showing the angular quartz grains.

5 Good shale from the Middle coal-measures of Lancashire The silica contained in this shale is wholly of a colloidal character. The black streaks are fragmentary plant impressions (carbonaceous matter)

6 Dust from No 5, this shows the flaky nature of the particles

All photographs are taken under polarised light with a magnification of 40 diameters.

SUBSTITUTES FOR STONE DUSTS

The following materials have been submitted as substitutes for stone dusts :

Cement Works Stone Dust Substitute.

	Per cent Composition
Silica	56·99
Ferric oxide	4·39
Alumina	21·41
Calcium oxide	2·60
Magnesium oxide	2·09
Sulphur trioxide	1·89
Carbon dioxide	nil
Water	0·54
Alkalis and loss	3·48
Organic matter and combined water	6·61
	100 00

Chance's Mud (Stone dust substitute)

Iron	0·79
Sulphide sulphur	0·12
Total sulphur	0 94
Water	5 47
Loss on ignition	45·08

The Weathering of Shale (Sinnatt and Grounds unpublished work).

With a view to increasing the efficiency of the plant for the grinding of shale, and also to determine whether the shale dust can be modified in form, experiments were carried out to determine the effect of the influence of weathering upon certain shales. It is well known that on exposure to the atmosphere shale splits up into laminated shapes, and that this degradation continues the longer the shale is exposed to the air The action depends upon the absorption and expulsion of moisture, and is known to have the maximum effect during the winter and autumn of the year. The experiments, which covered a period of some months, were sufficient to show that if the shale is allowed to weather for a certain length of time great economy is effected in the grinding of the material It would appear that by allowing the material to weather it is possible to obtain fine stone dust in a form which has different physical characteristics than when the material is simply ground without weathering. The stone dust made from the weathered materials appears to be spherical in shape, whereas when it is pulverised from the lump it tends to be more angular and flaky In view of the evidence suggesting that dust having an angular sharp edge tends to increase the liability to disease among the workers, it would appear that weathering previous to grinding would be desirable. Further experiments reveal the fact that if shale is submitted to artificial weathering (i.e., alternate heating and cooling) the degradation takes place much more rapidly. The following is a brief outline of the experiments which were carried out :

A kilogram of fine stone was prepared of 1/10 to 1/4 inch mesh sieve by breaking down large pieces of a typical sample of shale. This shale was received about three days after being mined, and was prevented from coming into contact with the air in which the experiments were commenced The kilogram of stone was thoroughly sieved, freed from finer material than 1/10 inch mesh, and nine average portions (100 grams weight each) of the material were weighed out into glass dishes of 4¾ inches diameter. In this way a very thin layer of shale was obtained. The dishes were exposed to the outside atmosphere, but protected from dust and rain for three, six, and up to twenty-four days. A sieving test and determination of moisture was carried out on each sample before and after grinding. The results of the trials are as follows :

Before grinding.

Days Exposure.	Rem on 1/10 Sieve. Per cent.	Rem on 1/30 (through 1/10) Per cent.	Rem. on 1/60 (through 1/30) Per cent	Rem on 1/90 (through 1/60) Per cent	Rem. on 1/200 (through 1/90) Per cent	Through 1/200 Per cent	Moisture Per cent.
0	·	·	·		·	·	
3	97·2	2·0	0·2	0·1	0·1	0·4	1·33
6	97·0	1·9	0·2	0·1	0·2	0·6	1·67
9	96·8	1·9	0·2	0·2	0·2	0·7	1·98
12	97·0	1·8	0·3	0·1	0·2	0·6	1·64
15	98·9	0·8	0·1	nil	0·1	0·1	1·77
18	95·8	2·2	0·4	0·5	0·2	0·9	1·52
21	92·2	3·5	0·6	0·4	0·6	0·8	1·9

After grinding 1 hour and 20 minutes in ball mill.

Days Exposure	Rem on 1/10 Sieve. Per cent.	Rem on 1/30 Sieve. Per cent.	Rem. on 1/60 Sieve Per cent	Rem on 1/90 Sieve. Per cent	Rem. on 1/200 Sieve Per cent	Through 1/200 Sieve. Per cent	Moisture Per cent.
0			··		··	·	··
3	83·38	9·43	1·70	1·00	0·8	1·7	
6	86·33	9·15	1·60	0·70	0·5	1·7	
9	81·35	7·15	1·95	1·55	2·40	5·60	
12	78·85	11·75	2·70	1·60	2·0	5·1	
15	65·7	5·0	2·2	1·5	8·5	19·1	
18	60·85	8·9	2·15	2·8	5·0	20·5	
21	60·1	3·65	1·25	2·4	5·5	27·1	
27	54·4	4·2	1·5	3·0	6·0	30·9	

A further portion of 100 grams was placed in a hot air oven, and heated to 105° C for one hour, cooled for one hour, and alternately heated and cooled in this manner three times. The results of this treatment are shown below :

Rem on 1/10 Per cent.	Rem on 1/30 Per cent	Rem on 1/60 Per cent	Rem on 1/90 Per cent	Rem on 1/200 Per cent.	Through 1/200 Per cent.
70·05	5·6	1·2	2·93	5·0	15·2

The mechanical details of the trial are as follows :

Grinding surface=1,080 inches per minute (slipping, pounding, and rolling)

Charge=500 grams rivet punchings (cylindrical, 0·65 inch diameter, 0·30 inch thick).

No of punchings per charge=45

Total grinding time=60 minutes, at 110 revs. per minute.

From the results obtained by alternately heating and cooling the crude stone, it will be seen that in six hours the quantity of fine dust passing through a 1/200 mesh sieve is approximately the same as that produced after 14 days weathering. Thus, the grindability of a stone may be greatly accelerated by exposure to alternate heat and cold, contrasted with the slow effect produced by natural weathering.

The authors wish to express their thanks to Miss H. Greenleaves, for help during the preparation of this bulletin.

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THE INORGANIC CONSTITUENTS OF COAL

PART III

THE CHEMICAL COMPOSITION OF IRON PYRITES FROM COAL

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1922

BULLETIN XII

PREFATORY NOTE

The Lancashire and Cheshire Research Association has for some time been engaged upon the study of the spontaneous ignition of coal as it applies to the seams in the Lancashire Coalfield and, in view of the great differences of opinion upon its fundamental causes, it has been felt that various factors in connection with the coal seams should be investigated.

In Bulletin 5, " Coal Dust and Fusain," and Bulletin 8, " The Inorganic Constituents of Coal," certain phases of the problem were examined; the present bulletin contains still another stage of the work, and consists of an examination of various forms of pyrites which have been encountered. It is hoped that at a later date it will be possible to publish the results of the microscopical examination of many samples of pyrites as carried out by Mr. J. Lomax in association with the present investigation.

The prevention of gob fires and the spontaneous ignition of coal, either in the coal store or in the holds of ships, would be of the very greatest benefit to the coal industry, and the report of the enquiry published by the Mines Committee (Departmental Committee on Spontaneous Combustion of Coal in Mines) only emphasises the great necessity for further investigations of the problem.

THE INORGANIC CONSTITUENTS OF COAL

PART III

THE CHEMICAL COMPOSITION OF IRON PYRITES FROM COAL

The present bulletin contains a description of a continuation of the investigation of the inorganic constituents of coal, and deals mainly with the chemical composition of various forms of pyrites which have been encountered.

The first publication on the subject dealt with the white partings (ankerites) which are an ingredient of most coal seams (Sinnatt, Bailey and Grounds. Bull. 8, Lanc. Ches. Coal Res. Ass). In a second communication (Sinnatt and Simpkin. J.Soc.Chem.Ind., 1922, XLI., pp. 164T-167T) the various forms in which iron is present in coal were described, and in two contributions to the discussion on Mr. Cecil Newton's paper on "Heating of the Goaf and the Steps taken in Conjunction therewith at Chanters Colliery" (Trans Inst Min Eng., 1922, XLII., p. 261) an investigation of the forms in which the iron was present in the material which heated in the goaf was described.

In view of the fact that the whole of the literature on the subject of pyrites was reviewed, it was felt desirable to include a bibliography of the chief papers dealing with the chemical aspect of the subject.

An exhaustive enquiry into the problem of the spontaneous combustion of coal in mines has been made by the Committee on the Spontaneous Combustion of Coal, and it is not considered desirable, therefore, to attempt to associate the results included in this bulletin with the subject of the spontaneous ignition of coal.

In the evidence taken before the above Committee there appears to be a general assumption that only two minerals containing iron and sulphur can exist in coal, viz., iron pyrites and marcasite. The two compounds are discussed as the only possible alternatives whilst definite chemical properties in relation to their mode of oxidation are assigned to each. Although the values given in this bulletin cannot be considered as sufficient to warrant broad generalisations, nevertheless they indicate that pyrites in coal is always associated with a considerable proportion of mineral matter, and that the specific gravity of the coal pyrites may differ considerably from ordinary pyrites. The inorganic matter associated with coal pyrites generally contains amongst other constituents iron carbonate (one specimen was found to contain 78 7 per cent. ferrous carbonate), the iron being present in the ferrous condition. Such a compound might undergo rapid oxidation, and its presence may account for the great readiness with which certain types of pyrites are known to oxidise

The ankerites present in coal (see p 14) also contain iron in the ferrous condition, and rapidly oxidise, especially in the presence of moisture and carbon dioxide.

Experiments have been carried out upon the rate at which different specimens of ankerite will undergo oxidation. These results will be published at a later date, but it may be stated that certain specimens have been found to undergo oxidation much more readily than others

It would seem that coal pyrites frequently contains a small percentage of the same constituents as the ankerites, but that the proportion of ferrous iron present in the pyrites is greater, in relation to the other constituents, than is found in the ankerites.

It is desirable to state at this point that the work is being continued, and that reservation is placed upon investigations which deal with the rate of oxidation of different types of coal pyrites and ankerites.

Description of Iron Pyrites and Marcasite.

Iron disulphide (FeS_2) occurs in nature in two isomeric crystalline forms, namely as pyrites and as marcasite. The two varieties exhibit differences in physical and chemical properties.

[*Iron Pyrites*

Iron Pyrites.

Iron Pyrites (FeS_2) occurs in the cubic and pyritohedral form, the faces of the cubes being frequently striated. It is found in massive formation, but also exists in granular, reniform and fibrous forms. As a rule it is hard, but brittle, breaking with a conchoidal fracture, and varies in colour from a bronze yellow to a pale brass yellow: specimens which have undergone superficial oxidation exhibit many shades of bronze, yellow, green, etc. According to E. S. Dana (Textbook of Mineralogy) pyrites readily changes superficially to limonite (a hydrated oxide of iron $2Fe_2O_3.3H_2O$). This action proceeds throughout the mass in the presence of bicarbonate of lime, the latter neutralising any sulphuric acid produced by the oxidation of the pyrites, the limonite may be finally converted into oxide of iron Fe_2O_3.

The specific gravity of pyrites varies somewhat according to different authorities, and the following are the values quoted:

Specific Gravity	(Dana)	4·96-5·10
" "	(Moses and Parsons) .	4·90-5·20

Marcasite.

This mineral, identical with pyrites in chemical composition, occurs as tabular crystals (orthorhombic system) which frequently exhibit twinning. The crystals are paler in colour than pyrites. It is stated to undergo oxidation more readily than pyrites, the surface deepening in colour even after a few hours' exposure to the air. Many varieties have been described, and the following terms are found in the literature:

"Radiated," "Cockscomb," "Spear," "Twin," and "Capillary" pyrites.

Its specific gravity is as follows:

Specific Gravity	(Dana)	4·65-4·90
" "	(Moses and Parsons) ..	4·60-4·90

Distinction between Pyrites and Marcasite.

Owing to the fact that pyrites and marcasite resemble one another so closely, it is difficult to distinguish them either by appearance, crystalline form or specific gravity. Many attempts have been made to estimate the two forms of iron disulphide in a mixture, and a method described by H. N. Stokes (U.S. Geol. Survey, Bull 186, 1901) may be cited as typical. This process depends upon the fact that when pyrites or marcasite is heated with an excess of a solution of a ferric salt the latter is completely reduced. The ratio of the sulphur oxidised to mineral decomposed, is definite and characteristic of each of the minerals, provided certain standard conditions have been established.

Owing to the large amount of extraneous matter associated with the specimens of pyrites examined by the authors, it was not found possible to apply the work of Stokes to the different specimens as the presence of extraneous substances influences the course of the reaction.

IRON PYRITES IN COAL

Many different types of iron disulphide occur in coal, varying both in physical appearance and chemical composition : certain specimens are extremely hard, crystalline and bright in colour, whilst others are soft, non-crystalline and difficult to distinguish from the coal substance.

This marked variation in the mode of occurrence of iron disulphide would point to the fact that certain varieties may be more prone to oxidation than others.

Although the literature contains many references to pyrites in coal in relation to its effect upon (*a*) spontaneous combustion, (*b*) the ash derived from the coal, and (*c*) its removal and recovery from the coal substance, little has been published upon the actual chemical composition and properties of different specimens of pyrites.

In this connection reference may be made to a paper by H. F. Yancey, " Some Chemical Data on Coal Pyrites " (Chem Met.Eng., 1920. 22. 105), in which the results of an investigation upon the pyrites associated with American coals are described, without, however, including a complete analysis of any of the specimens. The following table contains the specific gravity of various pyrites quoted by Yancey, together with the sulphur content :

Source.	Percentage of Sulphur.	Specific Gravity.
Tennessee	15·1	2·70
Illinois	25·5	2·89
„	29·7	3·62
„	42·0	3·99
„	44·0	4·41
„	46·7	4·09
„	48·9	4·32
Ohio	51·2	4·76

In view of the above table, Yancey comes to the conclusion that there is no relationship between the percentage of sulphur present and the specific gravity of the specimens.

An additional observation made by Yancey was that the pyrites from coal contained a smaller amount of arsenic than ordinary pyrites, whilst the phosphorus present varied from 0·003 to 0·083 per cent.

Source	Percentage of Arsenic.
Pennsylvania	0·056
Illinois	0·029
„	0·005
Ohio	0·005
Tennessee	0·015
Pennsylvania	0·039

The Chemical Composition of Pyrites associated with Coal. The pyrites associated with coal exhibits great differences not only in its chemical composition, but also in its physical characteristics. In the specimens examined by us, the actual amount of iron disulphide present was found to differ materially, whilst the inorganic constituents associated with the disulphide contained a variety of substances.

In view of the great variation in the mode of occurrence of pyrites, it has not been possible to analyse specimens of every type encountered owing to the difficulty experienced in separating them from the associated coal and mineral matter. This applies especially to the pyrites which occurs in microscopically small aggregations.

In the preparation of the specimens for examination it was necessary to separate the adherent mineral matter (both inorganic and organic) from the pyrites. It must be pointed out, however, that in many cases the pyrites was so intermingled with foreign matter that it could not be separated by ordinary physical methods.

The specimens of pyrites examined cover a wide range, from material which was found in large masses to pyrites which occurred in a fine state of division and which was difficult to separate from the coal. In order to separate this latter type of pyrites from the associated coal, the pyrites was coarsely pulverised and advantage taken of the difference in specific gravity of the pyrites and extraneous matter, the lighter material being floated off by treatment with chloroform. The separated mineral matter was washed finally in a stream of that liquid.

Description of the Specimens.

We have to thank Mr. J. Lomax of Bolton for providing us with a number of the specimens of pyrites. Most of them he has identified in the course of an exhaustive microscopical and palæobotanical study of the method of occurrence of pyrites in coal.

(1) *Solid Pyrites* (*Lancashire*).*

This was a solid piece of material of a somewhat heterogeneous character exhibiting a bright yellow colour streaked with darker markings. The bright surface undergoes superficial oxidation and then assumes many shades from deep bronze to green. A freshly broken surface exhibited only the dark and bright mottled appearance. When the material was treated with hydrochloric acid, the coloured surface rapidly dissolved with effervescence, leaving a bright, whitish yellow pyrites. This sample is remarkable in that a superficial examination might lead to the conclusion that it contained a high percentage of pyrites. It may be pointed out that it only contained about 60 per cent. of iron disulphide, and that the balance consisted of constituents the nature of which may be gathered from the complete chemical analysis given later (p. 13). This material may be contrasted with a sample obtained from the Pemberton 5 ft. seam, which, although similar in appearance, was found to contain over 90 per cent. of actual iron disulphide.

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* Seams which occurred in the Lancashire coal field are designated by name. Where it was necessary to obtain coals from other coal fields the seams are designated by a letter.

(2) *Solid Pyrites, Pemberton 5 ft. (Leigh, Lancashire).* This specimen occurred in the form of large lenticular nodules, which attained a size of one inch in thickness, 5 inches in length and 3 to 4 inches in breadth. The nodules were surrounded by shale of a highly carbonaceous character, which was replaced by pure coal in various regions. When the carbonaceous shale was replaced by coal, the band of pyrites was frequently thicker and became practically a continuous layer of material as distinct from the lenticles mentioned above. The pyrites possessed a whitish yellow colour, but had no definite crystalline form, except in a few isolated places where the crystals were cubical. Aggregations of a white substance could be detected, and when the specimen was treated with hydrochloric acid, these rapidly dissolved with effervescence leaving the yellowish white pyrites unaffected.

(3) *Solid Pyrites (Lenticular) (4 ft. Seam, Bolton, Lancashire).*

The lenticle was about 6 inches in length and varied in thickness to a maximum of 1½ inches. The colour was distinctly greenish, and a white incrustation surrounded the outer edge of the pyrites where it came into contact with the coal: this incrustation was visible as a band of varying thickness on the coal to a depth of about two inches. The separated pyrites was devoid of crystalline structure, but there were present occasional hair-like veins of a bright yellow colour. Hydrochloric acid was practically without action upon the specimen.

(4) *Cubical Pyrites (Wigan 5 ft. Underclay, Lancashire).* The specimens of pyrites were in irregular pieces of about ¼ inch diameter. They were found in an under-clay, minute particles of which still adhered to the material when analysed The pyrites was definitely crystalline in structure, brittle, and of a silvery gold colour

Upon analysis it was found to be practically pure iron disulphide, and, in addition, its specific gravity was higher than any of the specimens previously examined. The iron and sulphur were present in approximately the proportions occurring in iron disulphide FeS_2. The small amounts of other elements present may be assumed to occur in the clayey matter associated with the pyrites.

No trace of carbonate was found, whilst the amount of iron soluble in hydrochloric acid was negligible and was probably due to slight superficial oxidation.

(5) *Fibrous Pyrites (Doe Mine, Lancashire).*

This type of pyrites differed considerably from any of the above, in that it formed a strong network throughout the mass of the coal. It occurred chiefly parallel to the bedding plane of the coal and as veins of hair-like thickness at right angles to it. The colour was a dull yellow. When the pyrites was treated with hydrochloric acid no effervescence was observed.

(6) *Pyrites from Seam W.*

The pyrites occurred in the seam in dull masses surrounded by fibrous hair-like veins. The pyrites and the coal were closely intermingled, and it was difficult to separate them. It was observed that the pyrites, when separated, had a bright yellow colour, and contained ferric salts which were soluble in water. The coal associated with the pyrites was harder and more brittle than the general mass of the seam.

(7) *Pyrites from Seam X, Type A.*

This type of pyrites occurred mainly in thin scales of a bright whitish yellow colour, but fibrous layers could also be detected. When treated with hydrochloric acid no effervescence could be observed. An appreciable amount of iron dissolved in the acid without, however, affecting the appearance of the surface of the pyrites. The pyrites was more fragile than the types previously described. The material separated by flotation in chloroform possessed a dark greenish yellow colour and was almost devoid of crystalline structure.

[*Iron Pyrites*

(8) *Pyrites from Seam X, Type B.*
This type of pyrites occurred as a band of material varying from 1/16 to ¼ inch in thickness. It was composed of yellowish particles closely interlaced with coal and was distinctly soft in nature. It was attacked by hydrochloric acid with marked effervescence.

(9) *Globulites from Trencherbone Seam West* (*Lancashire*).
In addition to the previous types of pyrites, consisting of "solid, fibrous, stringy and flaky" varieties, another type, termed "globulites" (Lomax. Trans.Inst.Min.Eng., 1913-14, 46, 592 *seq*) from the structure of the aggregates, occurs in a number of seams dispersed through a particular horizon of the seam. In the Trencherbone seam this variety of pyrites was found in a band of coal close to the base of the seam, as small spheroidal globules approximately 1/32 of an inch in diameter The substance of which a unit was composed was reddish brown in colour and somewhat fragile. Microscopical examination showed that the outer shell in each of the small globules had a brighter appearance than the central portion. When a globule was treated with hydrochloric acid, a portion rapidly dissolved with effervescence whilst the residue became distinctly brighter and more yellow in appearance. The residue formed a small annular cup, from which the central material had been removed by the acid (Lomax. Minutes of Evidence before the Departmental Committee on Spontaneous Combustion, August 11th, 1914, p. 95.)

From the above brief description it will be gathered that the globules consist of two distinct substances, (1) comprising the outer shell and consisting of bright yellow material insoluble in hydrochloric acid and (2) the centre portion of each globule which was brown in colour and freely soluble in cold hydrochloric acid. The fact that this material dissolves with marked effervescence indicates that it contains a considerable proportion of carbonates.

(10) *Globulites, Seam Y.*
The present type of globulites was similar in form to that described above, but the colour was dull, brownish yellow as distinct from the red brown appearance associated with the Trencherbone globulites; except that the material was

harder, the properties of this specimen were similar to those of the Trencherbone globulites.

(11) *Globulites from Seam Z.*
The material was disseminated throughout the coal in small, hard, brownish spheres similar to those which occur in the Trencherbone seam, but somewhat browner in colour. When separated by means of chloroform, the globulites were seen to possess a dull brown colour with an occasional particle having a bright yellow lustre. When the material was treated with hydrochloric acid a slight evolution of carbon dioxide occurred. Subsequent examination indicated the presence of a large proportion of carbonates, but rapid evolution of carbon dioxide only occurred when the material was heated with hydrochloric acid.

Chemical Composition of the Specimens.
The following table contains the percentages of pyritic iron and sulphur found in each specimen. The specific gravity of the material used for the analysis was determined and is given in the last column:

Table 1.

Specimen.	Percentage of actual FeS_2 Present.	Percentage of Pyritic Sulphur.	Percentage of Pyritic Iron.	Percentage of Non-Pyritic Iron.	Specific Gravity.
1. Solid Pyrites (Lancashire)	56·66	30·22	26·44	9·77	3·588
2. Solid Pyrites (Pemberton 5ft.)	93·80	51·04	42·76	0·15	4·391
3. Lenticular	83·54	44·96	38·58	nil	3·360
4. Cubical	94·16	50·22	43·94	0·89	4·987
5 Fibrous Pyrites	83·19	44·37	38·82	1·94	3·249
6 Seam W	83·12	44·33	38·79	3·51	4·074
7 Seam X (A)	89·17	47·56	41·61	0·65	3·550
8 Seam X (B)	87·26	46·54	40·72	2·11	3·779
9. Globulites (Trencherbone)	73.41	39·15	34·26	3·92	—
10. Globulites (Seam Y)	77·12	41·13	35·99	2·83	3·664
11. Globulites (Seam Z)	4·59	2·45	2·14	35·85	3·420

The whole of the specimens with the exception of No. 3, contain an excess of iron above that required to form iron disulphide with the pyritic sulphur present.

In view of the action of ferric salts upon pyrites it was not possible to determine whether the excess iron was present in the ferrous or ferric condition, since upon treating the material with hydrochloric acid, any ferric iron passing into solution would tend to be reduced to the ferrous condition. The excess of iron has been recorded in the analyses as occurring in the ferrous condition. It probably existed as ferrous or ferric oxide or carbonate.

The following table contains the complete analyses of the five specimens which were considered typical:

Table 2—Complete Analyses.

No. of Sample.	1	2	3	4	11
Name of Sample	Solid Pyrites	Solid Pemberton 5 ft	Solid Pyrites Lenticular	Cubical Pyrites.	Globulite from Seam Z
Moisture .	0·64	0·50	1·21	nil	0·25
Insoluble Matter	0·69	0·85	0·21	0·61	0·35
Iron (Pyritic) .	26·44	42·76	37·63	43·94	2·14
Sulphur (Pyritic)	30·22	51·04	44·96	50·22	2·45
Iron (other than Pyrites as FeO)	12·56	nil	1·22	1·14	46·09
Aluminium Oxide	2·31	3·36	3·22	3·62	4·42
Calcium Oxide .	7·01	0·48	nil	0·09	3·38
Magnesium Oxide .	3·60	trace	0·84	0·54	4·57
Sulphur Trioxide	1·29	nil	1·90	nil	nil
Carbon Dioxide	10·23	0·38	0·99	nil	32·62
Carbon (Organic)	3·42	nil	6·04	nil	nil
Hydrogen (combined)	0·33	nil	0·75	nil	nil
Specific Gravity	3·588	4·391	3·360	4·987	3.420

The following conclusions may be drawn from the above values:

(1) The physical appearance, colour and hardness cannot be relied upon as an indication of the presence of a high percentage of iron disulphide: a number of the specimens examined were hard and exhibited a bright yellow appearance, but contained only a relatively small proportion of actual disulphide. Other specimens which were devoid of crystalline structure and possessed a dull greyish green colour, contained a high percentage of disulphide.

(2) The specific gravity affords no direct indication of the purity of the specimens, i.e., the amount of actual disulphide present is not proportional to the specific gravity.

It will be noticed in Table 2 that the composition of the foreign matter associated with the pyrites varies greatly. In two cases (1 and 11) a large proportion of iron is present either as oxide or carbonate, the latter being especially pronounced in the globulites from Seam Z—in other words—these particular globulites, though resembling in structure those from other seams, contain only a small proportion of actual iron disulphide, the material consisting chiefly of carbonate of iron (as distinct from ankerites).

With regard to the mineral matter, variations are encountered, some specimens containing a relatively large quantity of a single constituent, e.g., calcium oxide (Specimen 1), whilst it is absent from others as in Specimen 3

The Relationship of Ankerites to Pyrites.

Coal pyrites may vary from material which approximates to pure pyrites, to mixtures containing only a small proportion of iron disulphide. It is suggested that the oxidation of the iron disulphide itself may be influenced not only by its physical state, e.g., its specific gravity, degree of fineness and porosity, but also by the nature and composition of the foreign matter associated with it.

Table 3—Percentage Composition of the White Partings (Ankerites).

	Lower Mountain Mine	Arley	Ravine Mine.	Sapling Mine.	Hoo Cannel.	Rushy Park.	King Mine
Calcium Oxide .	27 40	28·56	29 94	42 79	30 08	28 76	30 84
Magnesium Oxide	13 33	11 51	16 15	0 41	11 18	8 74	5·76
Ferrous Oxide	14 56	9 81	4 80	13 07	14 16	16 23	18 42
Manganese Oxide	—	0 82	1 11	—	—	0 59	0 31
Carbon Dioxide .	45 21	41 52	44·35	41 88	44 58	42 56	42 03
Silica . . .	—	6 05	2 25	1 70	—	2·45	—
Ferric Oxide .	—	0 60	0 25	0·17	—	0 63	—
Pyrites . . .	—	1 11	—	—	—	0 09	2 47
Equivalent to							
Calcium Carbonate . .	48 93	51 00	53.14	76 41	53 70	51.36	55 08
Magnesium Carbonate .	28 30	24 07	33 65	0 66	23 48	18·28	12·10
Ferrous Carbonate	23 46	15 81	8 40	21 68	22 82	26 18	29·68
Manganese Carbonate .	—	1 33	1 80	—	—	0 96	0·50
Calcium Sulphate	—	—	0 44	—	—	—	—
Silica . . .	—	6 05	2 25	1·70	—	2 45	—
Ferric Oxide . .	—	0 60	0 25	0·17	—	0 63	—
Pyrites . . .	—	1 11	—	—	—	0·09	2.47

Attention may be called to a paper by Sinnatt, Grounds and Bailey (J.Soc.Chem.Ind., 1921, XL, 1-4T, and Bulletin 8, Lanc. and Ches. Coal Res. Assoc.), in which the authors give detailed analyses of the white partings (ankerites) occurring in Lancashire coal seams. The analyses of a number of specimens are contained in the above table.

It is a common occurrence for sheets of ankerites to be associated with pyrites. Frequently it would appear that one of these minerals may have replaced the other in a particular fissure in the coal. Thus, a continuous sheet composed largely of pyrites gradually changes to one consisting wholly of ankerites. This suggests that one of the minerals may have been formed from the other, for it must be recognised that the ankerites contain a considerable percentage of iron, and consequently it is reasonable to suppose that part of this iron may have been derived from pyrites or that pyrites may have been formed from it.

In order to gain some information on this point a specimen of Cannel (Lancashire) was selected on which a perfect sheet of material was deposited. This was about 2 inches wide, and varied from what appeared to be practically pure crystalline pyrites to material composed essentially of ankerites. The central portion of the sheet of material was examined with special care, and it was found that the crystals of pyrites were adjoining the cannel, whilst the larger portion of the ankerites formed a sheet on which these crystals might have been deposited.

With a view to determining whether the pyrites had been derived from the ankerite or vice versa, the middle portion of this sheet of material was carefully removed for about ½ inch in depth and ¾ inch in breadth, and the adjacent portion, which consisted of pure ankerites, was also separated.

In order to ascertain whether the percentage of iron present in the pure ankerite differed from that in the ankerite on which the pyrites occurred, the two specimens were analysed with the following results:

Percentage of iron in pure ankerite ...	8·58
Percentage of iron in ankerites associated with the pyrites	8·74

From the above it will be gathered that the ankerite is practically constant in composition throughout, despite the fact that in one portion it is covered with pyrites whereas in the other portion it is free from pyrites.

OXIDATION PRODUCTS OF PYRITES

The oxidation of pyrites in a mine is liable to occur continuously, being influenced by the humidity of the air, the temperature, the nature and physical condition of the pyrites and of the coal with which it is associated. Large solid accumulations of sulphates of iron are rarely found, but iron salts soluble in water are being gradually formed and give rise to the high iron content of mine waters.

Deposits of Iron Salts in Mines.

Four cases will be described as being representative of deposits formed under different conditions. In two instances, ferrous sulphate was found in large aggregations, whilst in the other two, the oxidation had proceeded further, the final product being the more highly oxidised ferric sulphate.

First Case.

Upon examining a portion of the roof of the Ravine Mine in which a local heating occurred, a crystalline stalactite about 8 inches long and 1 to 1½ inches in diameter was found. It was bright green in colour and entirely free from coal.

On exposure to the air for a few days the surface became covered with a greyish white powder due to loss of moisture. Longer exposure produced a deeper layer of this dehydrated salt on the surface of the green crystals.

A chemical analysis of the material showed that it consisted principally of crystalline ferrous sulphate $FeSO_4.7H_2O$ with a slight amount of adherent moisture, and other impurities. The specimen, as received, contained 18·7 per cent. of iron, corresponding to 93 per cent. of ferrous sulphate. After it had been allowed to stand for six months, the material was again analysed, the inner core and the outside layer being examined separately. It is a curious fact that although exposed to the air, practically no ferric salt had been formed during this period, the outer layer merely consisting of partially dehydrated ferrous sulphate. In addition to ferrous sulphate a small quantity of aluminium sulphate was present. The following table indicates the composition of the stalactite :

Table 4.

	Material as received	After standing Six Months		Pure Ferrous Sulphate.
		Core of the Deposit.	Outer Surface.	
Loss of Water at 105 °C.	not determined	38·53	24·52	38·88
Total Iron Fe .	18·7	19·42	23·41	20·09
Ferrous Iron Fe	not determined	19·32	23·23	20·09
Ferric Iron Fe .	"	0·10	0·18	nil
Aluminium Al .	"	0·66	1·62	nil
Sulphate SO_4 .	34·1	36·06	43·96	34·56

With regard to the above material, the following facts may be noted :

1. Free sulphuric acid was not present in the material.
2. The deposit was extremely pure, being chiefly ferrous sulphate.
3. Pure ferrous sulphate $FeSO_4.7H_2O$ loses 6 of its molecules of water of crystallisation (or 38·84 per cent.) when heated to 105° C, whilst the stalactite lost 38·53 per cent. when similarly treated.
4. The slightly excessive quantity of aluminium present on the outside of the material, viz., 1·62 per cent. as compared with 0·66, is probably accounted for by the fact that the outside may have been slightly contaminated with " foreign " matter.

The occurrence of such an accumulation is somewhat abnormal, and the most noticeable fact is that the oxidation of the pyrites has not proceeded further than the first stage, that is to say, no ferric sulphate had been formed. Ordinary ferrous sulphate exposed to the air under similar conditions became covered with white efflorescence which rapidly turned brown in colour, thus being quite different in its behaviour.

Second Case.

A deposit somewhat similar to the above has been placed at our disposal through the kindness of Mr. Whitehead of the Abram Coal Co, Ltd. It was found in a mine at Skelmerdale that is very liable to spontaneous combustion. The seam itself is about 10 ft. thick, the top coal containing pyrites and being liable to spontaneous combustion. The fires very rarely occur in the "strait," but take place in the wastes after pillaring has begun. The pyrites is very often associated with bands of fusain.

The crystals were found in the top coal associated with pyrites, and it is stated that there is little air in the places where they occur, as they were found in old "strait" roads which had been packed off, or had become swollen up. On allowing air to re-enter these old roads, the crystals changed to a white or creamy powder.

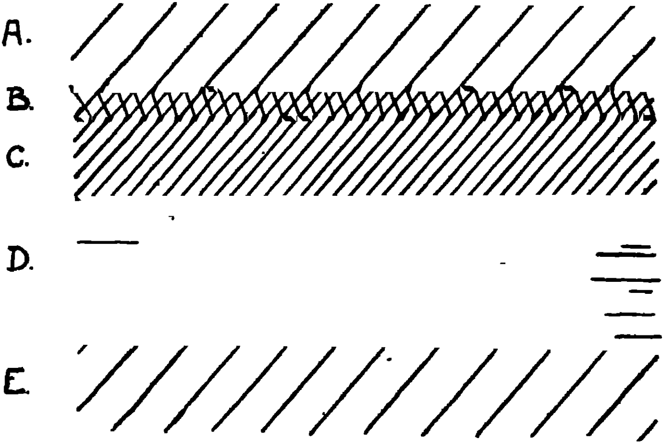
Upon examination, the crystals were found to consist almost entirely of ferrous sulphate, ferric salts being absent. Upon exposure, the white efflorescence formed on the surface, as in the case of the stalactite described above. It must be mentioned, however, that in the centre of a number of the masses of crystals, a quantity of apparently unaltered solid pyrites occurred. This pyrites was a bright pale yellow colour, of definite crystalline form and homogeneous in character. The ferrous sulphate and the pyrites adjoined one another, no intermediate band being visible. There was, however, present a small quantity (too minute for analysis) of a white substance which crystallised in fibrous crystals.

Third Case.

The deposit which consisted chiefly of ferric sulphate was found in a seam which shows a marked tendency to undergo spontaneous combustion. In addition, the ankerites or white partings which occur in large quantities in the coal, were oxidised to a degree which had not been noticed in any other seam examined. In other words, it would appear that conditions exist in the seam which facilitate the oxidation of any oxidisable substance present, and the fact that the reaction had proceeded to such an extent that ferric sulphate was produced would indicate that the oxidation is very pronounced.

The band of material which exhibits this tendency to undergo rapid oxidation lies approximately in the middle of the seam.

Diagram.



A is the top coal.

B is the incrustation which appears in the seam, approximately 3 inches above the band of material marked D. In between B and D is a layer of coal C.

D is a band about 5 inches wide composed of a soft shaly material which rapidly exhibits signs of weathering.

E is the bottom coal.

Analyses of the sections are given in the following table :

Table 5.

	A and C.	D	E.
Moisture	2·33	2·20	2·44
Ash	4·13	77·82	5·59
Volatile Matter	35·60	12·45	34 37
Volatile Org. Matter	33·27	10·25	31·93
Coke	64·40	87·55	65·63
Fixed Carbon	60·27	9·73	60·04
Nature of coke	friable, very swollen	non-coherent	friable, swollen

The yellow incrustation does not occur on a freshly cut face of the coal, but only appears after exposure to the air. The reaction appears to occur in a band running parallel with section D and about 3 inches above it, and the salt accumulates on the coal surface in the form of a pale yellow powder which gradually increases in amount with prolonged exposure. Analysis showed that the incrustation consisted principally of ferric sulphate.

The composition of the incrustation was as follows :

Percentage of iron (ferric)	15·6
„ „ sulphate SO_4	45·3

The occurrence of this ferric sulphate is in itself a distinct indication that very vigorous chemical action occurs, at a point between the top coal and the layer D. Fortunately, it was possible to examine part of the seam which had not been worked for several years. It was found that the band of coal C had become completely impregnated with the yellow ferric sulphate, which had also spread into the layer of shale D, the latter becoming soft and friable. This can be seen from the analytical figures given below, which prove that the percentages of iron and sulphur in the freshly mined material were lower than those found in the material which had been exposed for some time.

The composition of layer D was as follows :

	Newly Mined Sample.		Exposed in the Mine.
Percentage of iron ...	1·59	...	2·84
„ „ sulphur ...	1·08	...	1·61

It will be seen that the percentages of iron and sulphur had both increased considerably in the weathered seam—a fact which can only be due to infiltration (probably in aqueous solution). It may be stated that the layer of shale D which had been exposed in the mine was distinctly acid in character, whilst the freshly mined sample was absolutely neutral. The formation of the ferric sulphate, coupled with the fact that sulphuric acid is simultaneously produced, considerably assists in the disintegration or weathering of the coal.

Fourth Case.

In a paper by Mr. C. Newton (Trans.Inst.Min.Eng., 1922, XLII, 261) which contains an account of a deposit known locally as Batty, which occasionally occurs in the Arley Mine and which was the cause of a marked heating in the goaf, it was found that if the fine material was separated and removed from the pit before the Batty was put into the goaf, the coarse material showed no tendency to fire. As will be seen from the analyses quoted later, the Batty contained a high percentage of ash and consisted of material which rapidly disintegrated on exposure to the air.

In view of the previous work we had undertaken upon the forms in which iron occurs in coal, it was thought that the composition of the fine material of the Batty might differ from the coarse. An examination was, therefore, carried out with the object of ascertaining the nature and distribution of the iron compounds present in both the fine and the coarse material, and the following are three analyses of the Batty taken at intervals of about one month, together with an analysis of Arley coal.

Table 6.

	(1).	(2)	(3)	Arley Coal.
Moisture	2·2	2·4	2·60	1·92
Ash	25·6	38·5	24·75	1·75
Volatile Matter	29·0	26·2	31·52	35·34
Vol. Org. Matter	26·8	23·8	28·92	33·42
Coke	71·0	73·8	68·48	64·66
Fixed Carbon	45·4	35·3	43·73	62·89
Sulphur	3·5	5·4	7·73	1·45
Colour of ash			reddish brown	
Swollen (coke)			× 1½	
Nature of coke			dull, moderately strong	

The Batty was sieved, and that portion remaining on a 1/10 mesh sieve, together with that portion which passed through a 1/200 mesh sieve were examined separately with the following results :

	Complete Sample	Above 1/10.	Below 1/200
Water soluble (Ferrous) .	0·618	0·619	1·561
Water soluble (Ferric)	0·345		
Hydrochloric Acid soluble (Ankeritic) . . .	0·567	0·503	0·884
Nitric Acid (Pyritic)	4·632	5·271	2·051
	6·162	6·393	4·496

Distribution of The Iron.

	Complete Sample	Above 1/10.	Below 1/200
Water soluble (Ferrous) .	10·02	9·68	34·72
Water soluble (Ferric) . .	5·60		
Hydrochloric Acid soluble	9·20	7·87	19·66
Pyritic	75·18	82·45	45·62
	100·00	100·00	100·00

Quantitative Sieving Test.

Mesh of Sieve.	Percentage
On 10 Mesh .	. 64·9
10-90 Mesh . . .	28·0
90-200 Mesh	2·6
Through 200 Mesh	. 4·2

Analyses of the Fractions.

	Above 1/10	Below 1/200.
Moisture . . .	2·50	4·76
Ash . . .	29·50	16·48
Volatile Matter . .	30·48	37·27
Volatile Organic Matter . .	27·98	32·52
Coke	69·52	62·72
Fixed Carbon	40·02	46·24

The above determinations were carried out upon Specimen 3 in Table 6 (p. 21).

For purposes of comparison the approximate analysis of the Arley coal in which the material occurred is given in column 4 in Table 6. The forms in which the iron is present in the Arley are as follows :

Arley.

Percentage of iron	0·612	
Water soluble iron ..	2·15	per cent. of total iron.
Hydrochloric acid soluble iron ...	5·55	„ „ „ „
Pyritic iron ...	83·00	„ „ „ „
Silicate iron ..	9·92	„ „ „ „

In the interpretation of the above results, it must be pointed out that if a portion of the iron in the coal has been converted into ferric sulphate, when the coal is treated with water in order to determine the amount soluble, the solution of ferric salt produced will react with the iron disulphide (pyrites) present in the material and yield an additional proportion of iron soluble in water.

From a number of observations we have made upon the action of coal upon aqueous solutions of ferric salts, it has been proved that the production of ferric salts cannot be expected where the coal substance is in contact with a solution of the iron salt, as the coal reduced the ferric salts to the ferrous condition. At the same time it is clear that the fine portion of the Batty contains an abnormal amount of iron which is present in a form soluble in water.

It may be assumed that this soluble salt consists of sulphates of iron formed by oxidation of the pyrites, the ferrous sulphate produced tending to oxidise further to ferric sulphate. The ferrous salt would be liable to undergo oxidation except where it is surrounded by or in contact with the coal substance. Since ferric salts are present in considerable quantities in the Batty examined, it would appear that the carbonaceous material in contact with the Batty has undergone considerable oxidation and that possibly it has reached the stage at which it is incapable of further reducing ferric salts. On the other hand the ferric salt may not be in contact with the coal.

It is suggested that the production of iron salts which are soluble in water may form the intermediate reagent between the air and the coal substance In other words, in a mass of the coal where a certain proportion of water is present, the oxidation and reduction of the ferrous sulphate may proceed with the ultimate result that the coal substance is being continually oxidised, the iron salt acting catalytically.

A brief consideration of the four examples quoted above indicates that it is difficult to define the conditions under which any one of them was formed. It must be assumed that they were produced largely by the oxidation of pyrites, but it is not possible to foretell whether ferrous sulphate or the more highly oxidised ferric salt will be the end product.

The material (example 1) from the Ravine Mine exhibits practically no tendency to oxidise on exposure to the air, and in view of this, the factors which have caused the formation of ferric sulphate in the other deposits are not clear.

In most of the cases in which the pyrites had undergone oxidation, the material surrounding it was not pure coal, but usually highly carbonaceous shale. This association is not accidental, and it is suggested that the presence of such material containing pyrites of a type which undergoes oxidation may constitute one of the chief factors contributing to the heating of certain seams in the goaf.

The above results are of importance in connection with their bearing upon the following subjects:

1. The spontaneous ignition of coal.
2. The storage of coal.
3. The composition of pit waters and of the ochre deposits from such waters.

The difference in composition of the pyrites occurring in coal seams and the nature of the products of oxidation formed in coals liable to undergo spontaneous ignition, would indicate that the inorganic constituents are probably of great importance from the point of view of the storage of coal.

With regard to the composition of pit waters and of drainage water from colliery waste, it is well known that such waters frequently exhibit an acid reaction and are strong corroding agents. This is due not only to the direct formation of free sulphuric acid by the oxidation of pyrites as mentioned above, but also to the fact that iron salts readily hydrolyse in water with the deposition of basic iron compounds of indefinite composition and the formation of a solution which possesses distinctly acid properties. Consequently unless a very large quantity of bases are present which would tend to neutralise the acid formed, the formation of water soluble iron sulphates will result in waters possessing acidic properties.

Oxidation of Pyrites.

T. F. Winmill (Trans Inst Min.E., 1914. 51. 500) states that when pyrites oxidises to ferrous sulphate the reaction may be represented by the equation:

(1) $2FeS_2+7O_2+2H_2O=2H_2SO_4+2FeSO_4$

whilst the following equation may be taken as indicating the oxidation when a ferric salt is produced:

(2) $4FeS_2+15O_2+2H_2O=2Fe_2(SO_4)_3+2H_2SO_4$

If, however, the pyrites oxidises completely at a temperature approaching a red heat, the final products are sulphur dioxide and ferric oxide according to the equation:

(3) $4FeS_2+11O_2=2Fe_2O_3+8SO_2$

In all probability the reactions represented by equations (1) and (2) do not indicate the real course of the oxidation of pyrites, since secondary reactions increase the complexity of the products. The last reaction cannot proceed under the normal condition of oxidation occurring in coal except when the coal is being burned.

From analytical figures quoted above, it is shown that pyrites is usually accompanied by varying amounts of bases or carbonates which will react with any sulphuric acid generated by the oxidation, whilst the oxidation of the ferrous to ferric sulphate would tend to yield a basic ferric sulphate.

According to Evans (Min. Mag, 1900 12 371) iron pyrites in the absence of carbonate or carbon dioxide oxidises to yield ferrous sulphate which in turn is slowly converted into limonite $2Fe_2O_3.3H_2O$ (hydrated ferric oxide). Since this oxidation is retarded by the presence of sulphuric acid which is formed during the first stage, the degree to which the conversion of the ferrous sulphate to the ferric state will proceed is influenced by the presence of bases which would neutralise the acid produced and thus facilitate the reaction. The retarding effect of sulphuric acid is also assisted by the presence of chlorides and sulphates of certain metals, e.g., sodium, potassium and magnesium.

If ferrous sulphate is formed, the subsequent oxidation it will undergo is also influenced by the moisture content of the surrounding medium, e.g, a dry atmosphere retards the oxidation whilst a humid one has an accelerating effect.

Evans (loc. cit.) states that in the presence of carbon dioxide or carbonates, the sulphate is not formed as an intermediate phase, but a readily oxidisable carbonate is produced which subsequently passes into hydrated ferric oxide, especially in the presence of moisture. This affords a possible explanation of the quantities of oxide and carbonate of iron associated with some specimens of pyrites and the absence of all but mere traces of water soluble iron, i.e, sulphates.

The process of oxidation is influenced by the physical nature of the pyrites, finely divided material being more prone to rapid oxidation than lump or solid form, whilst the temperature and the amount of air and moisture in contact with the material will obviously influence the rate of oxidation. It will be noticed that for the formation of both ferrous and ferric sulphates a definite amount of moisture is required.

In the first case, i.e., when ferrous sulphate results, the moisture required amounts to 15 per cent. by weight of the pyrites oxidised, whilst if the sulphate becomes hydrated a further 105 per cent. of water is necessary. Reference is made to this observation in view of the fact that specimens of pure crystalline ferrous sulphate containing the full amount of water of crystallisation have been found in coal seams (see p. 16).

In this connection, mention might be made of an extract from a paper by R Threlfall (J Soc.Chem Ind., 1909. 28. 759): "I have been informed by Mr. Savage, a member of the 2nd N.S.W. Commission on the Spontaneous Combustion of Coal that at the Mootooroo Mine in South Australia there was a form of pyrites which rapidly decomposed, forming a pungent dust even in the exceptionally dry air of that district."

From this it would appear that oxidation occurred with only a small proportion of water present.

S. W. Parr (The Effect of Storage upon the Properties of Coal. Univ of Illinois, Eng Expt.Statn., Bull. 97, 1917) has carried out experiments upon the increase in the amount of sulphate in coal during storage. From his experiments he draws the following conclusions:

(1) Oxidation of the pyritic sulphur occurs at room temperature, the action being more pronounced with fine than with coarse material.
(2) Oxidation is more pronounced where the moisture and pyritic content of the coal are high.
(3) Fineness of division of the pyrites and its physical conditions influence the oxidation.

The above results should be borne in mind in the light of the oxidation occurring in one of the seams examined by the authors (*vide supra*).

If through oxidation or other causes, the coal substance loses the power of reducing ferric salts, then the latter will react with any pyrites present as soon as a small quantity of ferric salt is produced, with the result that the oxidation of the pyrites will commence, the presence of moisture and air facilitating the process. The reaction is represented by the following equations:

$$FeS_2+Fe_2(SO_4)_3=3FeSO_4+2S$$
$$2S+6Fe_2(SO_4)_3+8H_2O=12FeSO_4+8H_2SO_4$$

It will be seen from the above that the ultimate products of the reaction are ferrous sulphate and sulphuric acid, the former, under suitable conditions, oxidising to ferric sulphate.

The same results have been obtained experimentally by T. J. Drakeley (Trans Chem Soc, 1916. 109 723). He subjected pyrites to a current of moist air in a tube 140 cm. long, heated externally by steam so that the air rose from 15-18° C. on entering to 36-39° C. at the outlet. The pyrites under these conditions oxidised to ferric sulphate, but in the presence of powdered coal ferrous sulphate was formed.

Further experiments by Drakeley indicated that the admixture of iron pyrites with coal caused the absorption of oxygen at room temperature to be more vigorous at first, but ceased to have any effect after a time.

The reduction of ferric sulphate to ferrous sulphate by contact with the coal substance was suggested by Richters as early as 1869, the iron acting catalytically in the oxidation of a portion of the coal substance When this body or bodies became oxidised, the iron salt would cease to function as a catalyst and finally become completely oxidised to the ferric state.

In a series of experiments, the results of which will be published at a later date, the authors have examined the quantitative reduction of solutions of ferric chloride by means of coal; the coal substance readily undergoing oxidation whilst the ferric salt is reduced.

Heat Evolved by the Oxidation of Pyrites.

It is not intended to enter into the problem of the effect of the heat evolved when pyrites oxidises in air, upon the liability of the coal to undergo spontaneous combustion. It is clear, however, that if there is a certain amount of pyrites or other oxidisable inorganic substance present in the coal in a finely divided state, and the conditions are such that this material oxidises, the heat evolved will raise the temperature of the mass even if only to a small degree.

As a result of the work of Haldane and Meachem (Trans.Inst.Min.Eng, 1898. 16. 457), E. E. Sommermeier (J.Amer.Chem.Soc, 1904 26. 566 and 764), S. W. Parr and F. W. Kressman (Univ. of Illinois, Eng Expt.Statn., Bull. 16, 1910), and T. F. Winmill (Trans Inst Min.Eng., 1916. 51. 500), the heat evolved by the oxidation of pyrites can be stated with a fair degree of accuracy, although secondary reactions occurring during the process have not been investigated.

When pyrites oxidises according to the equation:

$$2FeS_2+7O_2+2H_2O=2H_2SO+2FeSO_4$$

heat is evolved equivalent to 623 K (K=1 large calorie of 1000 small calories), but owing to the effect of secondary reactions the heat evolved will be somewhat greater than this. In considering this subject the time taken for the oxidation is the determining factor: if the oxidation occurs in a relatively short space of time, the heat developed is not dissipated throughout the mass owing to the poor heat conductivity of the coal. If, however, the oxidation proceeds extremely slowly the heat generated, though actually the same in amount, does not have the same effect.

2 gm. molecules, i.e, 240 gms. of pyrites, when completely oxidised generate 623,000 calories of heat, i.e., sufficient to

raise the temperature of a mass of coal containing 1 per cent of pyrites

$$\frac{623{,}000}{240 \times 100 \times 0\ 35} = 74° \text{ C}$$

assuming the specific heat of the coal to be 0 35.

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The authors wish to express their thanks to Miss H. Greenleaves for help during the preparation of this bulletin.

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The following bulletin was recently issued, Paper Wrapper, 2/- net:—

XI. A CONTRIBUTION TO THE STUDY OF THE STONE DUSTING OF MINES, Part II; by F. S. Sinnatt, M.B.E., M.Sc. (Tech.), and A. McCulloch, A.I.C.

and the following are in preparation:—

THE ANALYSIS OF MINE GASES (illustrated); by F. S. Sinnatt and L. Slater.

THE CONTROL OF COAL WASHING; by F. S. Sinnatt and C. G. Wood.

THE METHODS OF STUDY OF A COAL SEAM; by F. S. Sinnatt.

THE PREPARATION OF THIN SECTIONS OF COAL FOR MICROSCOPICAL EXAMINATION (illustrated); by J. Lomax and J R. Lomax.

Messrs. H. F. & G. Witherby will have pleasure in registering the names of those interested in forthcoming bulletins, and in notifying the issue of each as it occurs.

THE DETERMINATION OF CARBON MONOXIDE IN VITIATED AIR

INCLUDING THE

ANALYSIS OF MINE GASES

By F. S. SINNATT, M.B.E.
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1923 BULLETIN XIII

THE DETERMINATION OF CARBON MONOXIDE IN VITIATED AIR

INCLUDING THE ANALYSIS OF MINE GASES

In the course of a number of investigations it has been necessary to examine the methods available for the determination of small volumes of carbon monoxide in vitiated air.

This bulletin contains a brief description of the methods which have been found to yield satisfactory results.

The vitiated air (containing carbon monoxide) has been derived from the following:

(1) The air from coal mines.
(2) The waste gases (air) from coal and gas fires and gas heated appliances (gas irons), etc.
(3) The gases produced during experiments upon the oxidation of coal.

A careful examination of the results and of the methods of analysis available has suggested the possibility of dividing these gases into the following types:

(*a*) In which the sample is small in volume and consists essentially of air containing small percentages of carbon monoxide, etc., associated with other constituents, and of which a complete and accurate analysis is necessary.
(*b*) In which large volumes of gas are available and the percentage of carbon monoxide present is lower than 0·02.
(*c*) In which large volumes of gas are available, but the percentage of carbon monoxide may vary within wide limits, or a determination extending over some considerable period is necessary.

Under the heading of (*a*) there occur probably the greater number of gases to be examined, for they will consist of mine gases and to a lesser degree air which is secured from the artificial oxidation of coal in the laboratory* and vitiated air from coal fires, coke fires, gas fires and other industrial processes.

The question of the analysis of mine gases is of considerable importance.

It is recognised that in general the only constituents it will be necessary to determine in the normal air from mines are carbon dioxide and methane.

It is not proposed in this bulletin to describe the determination of the two latter compounds; this aspect of the problem has been fully dealt with by Dr. J. S. Haldane.* He describes his original apparatus designed for the determination of methane and carbon dioxide. It is known, however, that there are abnormal cases in which it is necessary to determine the percentage of carbon monoxide occurring in the air of mines. The methods described here are designed with a view to the examination of such gases.

A knowledge of the exact amount of methane in the air and the variation which this undergoes under different conditions of the ventilating system is of importance. The values form a direct measure of the efficiency of the ventilating system, especially if samples are examined from "local places." The accurate determination of the methane over a period during which the ventilation undergoes slight pre-determined variations, gives a clear statement, by interpolation, of the rate at which methane accumulates in any position in the pit. As a rule this information is not available.

It has long been recognised that carbon monoxide is an essential product of the oxidation of coal (Wheeler and Rhead, Proc.Chem.Soc 1913 29. 51-82), and in more recent papers J. Ivon Graham (Trans.Inst.Min.Eng., Vol. LX., page 222) has proved that the presence of carbon monoxide in mine air may be associated with the spontaneous oxidation of coal, and further he has shown that the presence of carbon monoxide above certain normal values must be considered as an absolute indication that abnormal heating is proceeding in some part of the mine (goaf).

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* Methods of Air Analysis. J. Scott Haldane, M.B.

The following figures are given by J. Ivon Graham (*ibid.*):

The Normal Production of Carbon Monoxide in Mine Air

Area.	Percentage of Constituent.				
	CO_2	Combustible hydrocarbons	Oxygen	Nitrogen.	CO.
Yorkshire					
Barnsley Seam District No 1 Return ..	0·11	0·92	20·50	78·47	0·003
Lancashire					
Return from Four Foot and Rams Seam	0·35	0·85	19·81	78·99	0·004
Fifeshire					
Return from Five Foot Seam	1·93	0·01	18·47	79·59	under 0·0005
Staffordshire					
Return from North District	0·23	0·94	19·78	79·04	0·0095
Return from South District	0·24	0·76	19·89	79·11	0·011

During the oxidation of coal, products other than carbon monoxide are encountered in the issuing air (e.g., ethyl alcohol and acetone). Although the amount of these two oxidation products is extremely small, conditions may arise during the oxidation of coal which cause a maximum production of these two compounds, and in such quantity that during the subsequent combustion of the combustible hydrocarbons there may be a slight variation in the carbon dioxide/water ratio sufficient to prevent an accurate determination of methane, carbon monoxide, etc.

The amounts generally present are so small that they cannot be determined by ordinary gas volumetric methods, and the methods described in this bulletin are not suitable.

It may appear that no such test as the analysis of the air is necessary to replace the identification by means of the odour which is so characteristic of incipient heating in the goaf, but the smell of "gob stink" tends to permeate the whole of the workings and consequently the detection of the position of the heating is frequently a matter of difficulty It would appear, therefore, that rapid analysis of the air from any locality (goaf) would yield a positive indication of the intensity and approximate position of the zone of heating

The properties of carbon monoxide are too well known to need a lengthy description; many experiments have shown that even such an amount as 0·01 per cent. may have a marked influence upon the health of the person who is inhaling it continually, whilst when the percentage reaches 0·1, the atmosphere must be considered to be distinctly dangerous and human beings will be poisoned in a short space of time.

The subject is one with many aspects, but it is recognised that the human frame may become immune to small percentages, although the influence of the carbon monoxide must be considered to be that of a cumulative poison.

The following physiological effects are detailed by Veales (Trans Inst Min.Eng., Vol. LXIII., page 417. 1922) .

Percentage Carbon Monoxide in Air.	Physiological Effect.
0·114 .	Severe headache, weakness of the knees and difficulty in walking upright.
0·08 ..	Severe headache.
0·02 .	Caused temporary headache.

The effects described were the results of breathing air containing the carbon monoxide whilst the experimenter was at rest and breathing normally.

Further experiments indicated that the rate of absorption of carbon monoxide is increased fourfold when hard work is carried out.

It is clear that an accurate and rapid method of determining the carbon monoxide in mine air in addition to the determination of carbon dioxide and methane should be of value in the control of a colliery.

The analysis of samples of gas which may contain carbon dioxide, ethylene, carbon monoxide, methane and hydrogen cannot be performed in Haldane's original apparatus, and consequently a modified form must be employed.

[The Determination of Carbon Monoxide

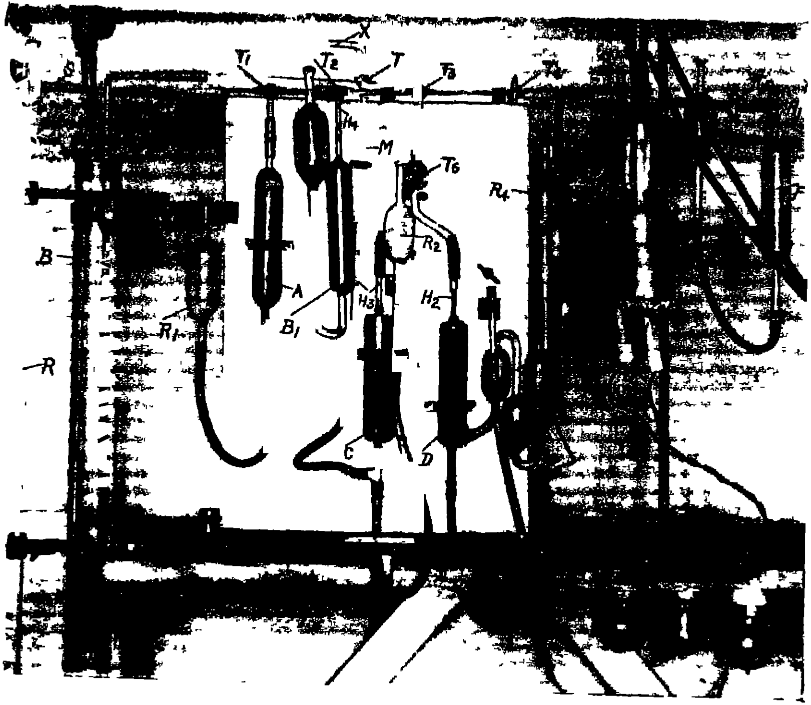

FIG 1

Experience has shown that the modifications necessary to the original Haldane apparatus can be readily carried out by local firms, and after a few preliminary attempts at manipulation a complete examination of a mixture containing the constituents mentioned above may be completed in three-quarters of an hour.

The apparatus to be described has been in continuous operation for three years, and although manipulated by various assistants it has maintained its efficient condition with relatively little attention.

The difference between the modified apparatus and that of Winmill (Trans Chem.Soc. 1914 105 1996) and Graham (J.S.C.I 1919. Vol. XXXVIII. 101T) is small and no claim to novelty is made

We wish to make it quite clear that the type of mine air that can be analysed by the present apparatus contains a greater amount of carbon monoxide or other constituents to be determined, than 0·02 per cent. Such a percentage of carbon monoxide would be quite abnormal in ordinary mine air, and if it is desired to determine a percentage lower than 0·02 per cent. or to determine the carbon monoxide in a normal mine air a method similar to those described by J. Ivon Graham (J.S C.I. 1919. XXXVIII. 101T) or one of us (Sinnatt. *Analyst.* April. 1913) must be adopted, which methods are examined later in this bulletin.

Description of the Apparatus.

The apparatus in its present form is shown in Fig. I, and in the description which follows of its manipulation the various taps to which reference is made are shown.

It will be seen that the burette and compensating burette are those of the standard Haldane apparatus C and D are absorption pipettes and P a combustion tube, which are standard on the normal Haldane apparatus. The pipettes A and B1, the iodine pentoxide tube U and the absorption pipette F are added to the apparatus in the manner described by Winmill (Trans.Chem.Soc. 1914. 105-1996)

Attached to the end of the main capillary on which are taps T1 to T4 is the iodine pentoxide reaction tube U, the details of which will be made clear by the following brief description ·

The iodine pentoxide is contained in a U tube, this latter being supported in a large boiling tube, the lower end of which is heated by an electrical heater as described by Graham (J.S.C.I. 1919 XXXVIII. 10T). The boiling tube contains water at such a level that when boiling, the U tube is surrounded only with steam.

By this arrangement a constant temperature is maintained in the iodine pentoxide tube, and steam escaping is condensed in the water condenser and returned to the boiling tube. The pipette F contains caustic potash, and attached to this is a levelling tube R3. At right angles to the main tube is attached the combustion pipette P, which is the standard combustion pipette of the Haldane apparatus.

Reagents

The reagents used in the course of the analysis are .

40 per cent. potassium hydroxide contained in pipettes C and F.

5 per cent. potassium hydroxide in pipette A

10 per cent. fuming sulphuric acid in pipette B1.

A solution of alkaline pyrogallol in pipette D. This solution is made up from a solution of 30 gms of pyrogallol in 100 c.c.s. of water, 20 c.c.s. of which are added to 90 c.c.s of 40 per cent potassium hydroxide in order to charge the pipette D.

Preliminary Manipulation

Before the sample for analysis is introduced it is necessary for the connecting capillary tubes to be filled with nitrogen and the levels of the liquids in the pipettes adjusted to set points whilst the gas in the compensating burette must be adjusted to atmospheric pressure

In order to fill the apparatus with nitrogen, air is taken into the measuring burette B, and by manipulating taps T7, T3 and T6 the air is passed into the absorption tube D by raising R. The air is allowed to remain in contact with the alkaline pyrogallol solution for about five minutes, and is passed into each of the pipettes in succession in order to sweep the air from the capillary connections. Finally the mercury is raised to tap T7 and air is swept out of the iodine pentoxide tube and eventually returned to the absorption tube D, where the oxygen present is removed. The tap T5 is then closed, T7 is opened again and the nitrogen is drawn from the absorption bulb D into B. The tap T6 is then turned to connect with absorption pipette C This is swept with the nitrogen which is then returned to D. After the absorption of the oxygen the nitrogen is finally expelled from the burette B through the inlet tube S. The levels of the liquid in each pipette A, B, P and F should have been adjusted to marks just below the corresponding taps T1, T2, T4 and T5. The connecting capillary tubes are now filled with nitrogen

It is not proposed to discuss the function of the compensating tube N, since this has been previously described by Dr Haldane (*ibid*). It is sufficient to state that at the commencement of every analysis the tap T is turned so that connection is made between the compensating tube N, the tube M and the atmosphere The level of the caustic potash solution in M is adjusted to H3 by raising or lowering R2. The tap T is then turned to connect only M and N.

The electrical heater EH is now adjusted and the liquid in the boiling tube maintained at gentle ebullition for 30 minutes in order to establish uniform temperature conditions in the iodine pentoxide tube At the end of this period the caustic potash in the absorption tube F is adjusted to the height H1 by opening tap T5 and carefully lowering R T5 is then closed Finally connection with C through T6 and T3 is secured and the levels of the two liquids accurately adjusted to H3 by raising or lowering R and R2.

Tap T4 is closed and the apparatus is now ready for the reception of the sample.

Introduction of the Sample for Analysis

The gas to be examined is admitted into the graduated pipette B through the side tube S

It is possible that the sample will arrive in various types of containers, and the exact method of manipulation preparatory to the admission of the gas will depend upon the form of the container It should be insisted upon, wherever possible, that the sampling tube should be of the accepted type of gas sampling tube of cylindrical form of from 100 to 250 c.c.s. capacity, and closed at both ends by a well ground three-way tap.

Assuming that this is the type of container the sampling tube is held in a vertical position, one exit at the top being attached to the inlet tube of the graduated pipette, and one inlet at the lower end to a small reservoir of mercury, each by a short length of pressure tubing.

The side tubes of the sampling tube being open to the air, they can be readily filled with mercury by manipulation of the taps, and in the case of the end attached to the graduated burette by simultaneously raising R.

After filling the connecting tubes the taps at either end of the sampling tube are rotated and a sample of the gas gradually drawn into B by lowering R, the mercury reservoir being adjusted at such a height as to prevent undue pressure.

The graduations upon the long stem of the burette B read from 15 c.c.s. to 21 c.c.s. It can be readily understood that if an insufficient volume of sample is drawn into B, after the completion of the final oxygen absorption the amount of residual nitrogen will be such as to render impossible a direct reading of the gas volume on the graduated portion of B As a result it is advisable to take not less than 18 or 19 c.c.s. as a sample

The sample having been taken into B the tap T7 is closed, the reservoir R is adjusted so that the surfaces of the mercury in B and R are as nearly as possible upon the same level The tap T7 is then rotated and connection made between B and C through T1, T2, T3 and T6. The water filling the water jacket round the measuring and compensating tubes B and N is then agitated by blowing several bubbles of air through (this agitation of the water is necessary before each reading) and the level of the caustic soda adjusted to H3 by raising or lowering R and R2. Finally the volume of the sample in B is noted. This volume is V

Method of Conducting the Analysis

The constituents are determined in the following order.

(1) Carbon dioxide

(2) Unsaturated hydrocarbons.

(3) Carbon monoxide.

(4) Combustible gases (methane and hydrogen).
(5) Oxygen.
(6) Residuals—nitrogen.

Carbon Dioxide

The reservoir R is slowly raised and the gas forced into C. It is allowed to remain for two minutes, removed by lowering R, and is again returned to C. This is repeated until no further diminution in volume is observed. The gas is finally withdrawn into B and the levels of the caustic potash adjusted to H3 as before. The volume occupied by the gas in B is then noted. This volume is V1.

Unsaturated Hydrocarbons

The tap T6 is then closed and T2 opened and the gas forced into B1 by raising R. When the level of the mercury in B has reached T7 the latter is closed and the tap T1 turned to connect directly A and B1. The gas is now slowly passed between B1 and A by raising and lowering R1.

By this method of manipulation any acidic gases from the fuming sulphuric acid do not make contact with the mercury.

This is recognised as a fruitful and troublesome source of error and delay in any apparatus involving direct contact of the mercury in the burette with any acid reagents.

This feature of the determination must be emphasised, for it confers upon the method advantages over other forms of gas analysis apparatus in that

(*a*) Complete absorption of unsaturated hydrocarbons is secured.
(*b*) The gas is freed from all traces of reagents and reassumes its original aqueous tension.
(*c*) Contamination of taps and the main caustic absorbent is avoided.

After a treatment of about five minutes the gas is entirely withdrawn from B1 into A, the level being adjusted at H4 in B1 and the tap T2 is turned so as to give a clear passage again. The gas is maintained in A for five minutes, at the end of which time any sulphur trioxide withdrawn from B1 has been absorbed, and as the caustic is very dilute (5 per cent.) the moisture content of the gas is restored. The tap T1 is then turned to connect A with C and the gas withdrawn into C. The level of the caustic in A is adjusted at H and tap T1 turned to its original position. The gas is then withdrawn from C into B and the levels of the caustic adjusted to H3 The volume of the gas in B is then noted This volume is V2.

Carbon Monoxide

Tap T6 is then closed and T4 and T5 opened to connect the U tube containing iodine pentoxide with B R is slowly raised until the level of the mercury reaches tap T7 T7 is then closed and T6 opened to connect F with C; the gas is then passed and re-passed through U by raising and lowering R2 and R3 alternately. After ten passages the level of the caustic in F is adjusted to H1 and the apparatus allowed to achieve its normal temperature, which occupies about five minutes. After the lapse of this time the caustic is finally adjusted to the level H1 by lowering R2 and the tap T5 closed The gas is then transferred to B, the levels H3 adjusted and the volumes in B noted. Tap T4 is then closed. This volume is V3

Combustible Gases

T6 is closed and the tap T4 is now opened to connect the combustion tube P with B and the gas passed into P by raising R. The combustion tube P contains a small platinum coil electrically heated to a bright orange colour, the current passing through the coil is adjusted by a variable resistance connected in series with the main supply. The reservoir R4 is raised and lowered very slowly and the gas passed frequently over the glowing coil until the combustion of hydrocarbons and hydrogen is completed. It is advisable during the combustion to raise the mercury above the level of the coil at intervals, and so short the heating circuit, in order to prevent the temperature of the glass becoming dangerously high and risking fracture. After combustion is deemed complete the current is switched off and the bulb P allowed to cool . when almost cold R4 is raised until the mercury level is returned to the point just beneath T4 and the latter is closed, the gas being returned to B T6 is now opened and the levels adjusted at H3 and the volume in B noted This volume is V4.

After determination of this volume the gas is returned to the combustion tube and the combustion continued until no further contraction is observed.

The gas in B is now passed into C in order to absorb any carbon dioxide produced during the combustion. The same procedure is repeated as in the first determination of carbon dioxide. After the levels have been adjusted to H3 the volume is noted. This volume is V5.

Oxygen

The tap T6 is now turned to connect B with D and the gas passed into D It is allowed to remain in contact with the alkaline pyrogallol for five minutes and then removed. It is again passed into D and retained in contact with the pyrogallol for a further two minutes or until the volume is constant and again withdrawn into B. It is finally returned to D and left for a further three minutes and then withdrawn into B and the level of the liquid adjusted to H2 by lowering R The tap T6 is then closed and the levels of the mercury in R and B adjusted at the same height. This adjustment is necessary preparatory to opening T6 to C in order to avoid the suction of liquid in C into the capillary tubes above T6 Finally T6 is opened to C and the levels adjusted to H3 and the final volume read This volume is V6. The residual gas is nitrogen

It must be clearly recognised that during the combustion of the gases in the combustion tube P a proportion of oxygen originally contained in the gas will have been required to bring about the oxidation of the hydrocarbons, etc. Corrections must be introduced (1) by calculating the amount of oxygen removed during the combustion or (2) by taking in a fresh sample of the original gas and carrying out only a determination of the percentage of carbon dioxide and oxygen by exposing the gas only to the action of the alkaline pyrogallol. If this latter course is pursued the last determination of the series resulting in the production of volume 6 will be omitted and the nitrogen determined by difference.

Calculation of Results

The volumes which have been noted during the analysis are :

In Vitiated Air]

Volume V
„ $V1$
„ $V2$
„ $V3$
„ $V4$
„ $V5$
„ $V6$

Volume V is the volume of the original gas

Volume $V-V1$ = carbon dioxide in the gas.

Volume $V1-V2$ = unsaturated hydrocarbons in the gas.

The reaction between carbon monoxide and iodine pentoxide results in a quantitative exchange of carbon dioxide for carbon monoxide, hence volume $V2-V3$ is the amount of carbon dioxide produced after the reaction, i.e, the amount of carbon monoxide in the original gas.

The contraction in the gas after combustion is due to the production of water, partly by methane and its homologues, partly by hydrogen, and the contraction after the absorption of carbon dioxide produced by combustion is due to the carbon dioxide produced by the combustion of methane and its homologues, hence, assuming the combustible gases present to be merely methane and hydrogen, then $V4-V5$ equals the volume of carbon dioxide produced by the combustion of methane, that is, equals the volume of methane

The amount of water which is produced is equal to twice the volume of the original methane—hence the amount of water due to the combustion of the hydrogen = $V3-V4-2(V4-V5)$, and the volume of hydrogen in the original gas is two-thirds the residual amount of contraction.

The volume $V5-V6$ gives the amount of oxygen remaining in the residual sample. As previously pointed out the amount of oxygen present in the original sample can be calculated from the percentages given for carbon dioxide and water above or they can be directly determined by the examination of another sample of the original gas. The percentage of carbon dioxide in the original gas being known, this subtracted from the oxygen as given by the fresh sample will enable the percentage of oxygen in the original gas sample to be calculated.

The final volume, $V6$, gives the amount of nitrogen present in the original gas If it is not considered sufficient to assume that the methane is present alone, but may be mixed with ethane, then hydrogen must be removed first, which removal can be conveniently carried out by maintaining in the boiling tube alongside the iodine pentoxide tube a further tube containing paladinised asbestos This will preferentially remove the hydrogen at a temperature of 100° C, leaving methane and ethane unoxidised, and this removal having been achieved the percentage of methane and ethane can be readily calculated from the analytical results showing the percentage of carbon dioxide and hydrogen produced on combustion.

The following is a typical example of the results secured from an examination of a series of samples taken in a coal mine in the Lancashire coalfield in which a gob fire was in progress.

These samples were taken over a period of six weeks, and two were taken in the roadway and two from a hole in the brick stopping.

Sample A.—Taken in roadway—process of flooding gob fire just begun.
Sample B—Taken at hole in brick stopping
Sample C—Taken at hole in brick stopping
Sample D—Taken in roadway.

The analytical results given by these gases are shown below ·

	Sample A. Per cent	Sample B. Per cent.	Sample C Per cent	Sample D. Per cent.
CO_2	0·10	0·40	0·34	0·25
Unsaturated hydrocarbons	0·05	0·10	0·09	0·05
CO ...	0·15	0·15	0·19	0·05
CH_4	0·39	0·64	0·39	0·44
H_2	0·25	nil	trace	nil.
O_2	18·21	18·88	17·50	18·72
N (by difference) ...	80·75	79·83	81·29	80·49

Where gases of the type enumerated under the heading (b) page 3, are to be examined the apparatus described by Graham* (J.S.C.I. 1919. Vol. XXXVIII. 101T) may be used.

This apparatus in its original form is intended as a portable type, available for use underground for the examination of the air of mines for the presence of small percentages of carbon monoxide.

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* Manufactured by Reynolds & Branson (Leeds)

The method of determination adopted is, i e, one in which a known volume of the air to be examined is passed over heated iodine pentoxide, other gases including hydrocarbons of the ethylene and acetylene series which would interfere with the reaction, having been previously removed.

The reaction tube containing the iodine pentoxide is maintained between the temperatures of 90-160° C In the original apparatus this is achieved by immersing the tube in oil at that temperature, the whole being contained in a Dewar (vacuum) flask.

For laboratory work the Dewar flask may be discarded and the necessary temperature secured by heating in a bath of molten paraffin wax

The reaction between the carbon monoxide and the iodine pentoxide results in a quantitative production of carbon dioxide and iodine according to the equation

$$I_2O_5+5CO=5CO_2+I_2$$

The iodine produced passes on in the stream of air, is absorbed in a dilute solution of potassium iodide and is finally titrated with a solution of sodium thiosulphate $\left(\frac{N}{500}\right)$.

In order to avoid error the air must be freed from all gases which are liable to adversely effect the iodine pentoxide with the production of iodine, and this condition is secured by passing it through a purifying train consisting of a wash bottle containing a 10 per cent solution of bromine in potassium bromide, a further wash bottle containing caustic potash solution and a drying tube containing calcium chloride, powdered caustic potash and phosphorus pentoxide

This train of apparatus was devised and used by Graham in his work upon the carbon monoxide content of mine air, but as the result of an examination which has recently been carried out by the writers (Fuel in Science and Practice, December, 1922), and which will be described shortly, this method must be modified in one particular This consists in the substitution of 10 per cent. fuming sulphuric acid for the bromine solution.

During a series of experiments it was observed that the amount of carbon monoxide present in the air was considerably higher than the accepted figure for the air of towns. The possibility of bromine traversing the final potassium hydroxide wash bottle was examined and eliminated by the addition of other wash bottles containing caustic potash.

Despite these additions the abnormal indications were still observed

Fresh reagents were employed and pure air passed through the apparatus. The gradual vitiation of these new reagents and the increase in the apparent carbon monoxide content is shown in the values quoted below. In the second column the percentage of carbon monoxide has been determined from the figures secured by the titration with $\left(\frac{N}{500}\right)$ thiosulphate of the iodine produced. Each sample of air consisted of 400 c.c.s.

Sample No.	Percentage Carbon Monoxide corresponding to Iodine liberated
1	nil.
2	nil.
3	less than 0·0014
4	„ „ 0·0014
5	„ „ 0·0042
6	„ „ 0·0056
7	„ „ 0·0028
8	„ „ 0·0056
9	„ „ 0·0049

From these results it is clear that the absorption of the bromine vapour by the strong solution of caustic potash results in the formation of some active volatile substance, which at the temperature of the experiment is capable of liberating iodine when brought into contact with iodine pentoxide.

This possibility was more fully investigated by making a mixture of 5 gms. of pure bromine in 100 c.c.s. of 40 per cent. potassium hydroxide solution. This was placed in a small Dreschels wash bottle and interposed between the drying tube attached to the iodine pentoxide tube and a sampling bottle capable of delivering a volume of 600 c.c.s. of air. The apparatus was so arranged that the air could be passed through the brominated potash and so over the iodine pentoxide or immediately into the brominated potash and then over the iodine pentoxide

A series of experiments was carried out under these conditions and the results are shown below.

In experiment A the air avoided the brominated potash, and in experiment B the air was passed first into the brominated potash and finally into the iodine pentoxide.

Experiment No.		Percentage Carbon Monoxide equivalent to the Iodine found
1	A	0 0014
	B	0·0140
2	A	0·0014
	B	0 0109
3	A	0·0014
	B	0·0124

Vol. of air in each experiment was 600 ·c c s

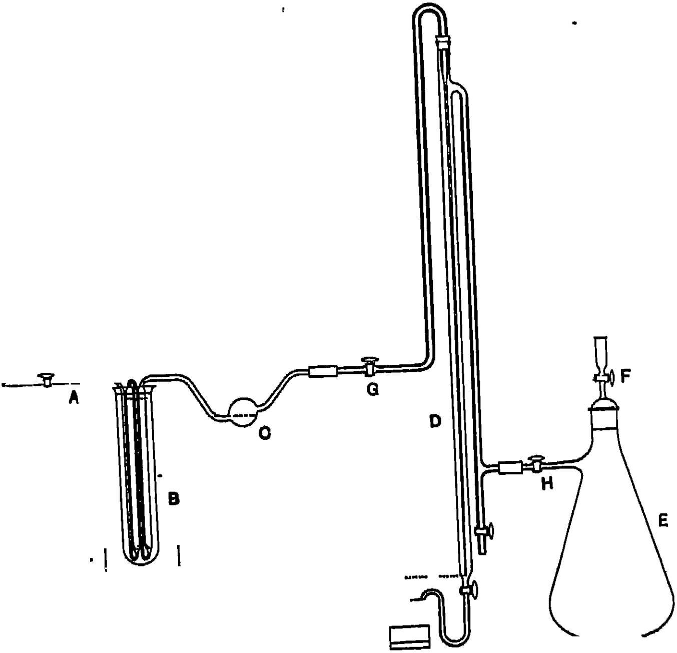
The above results are a clear indication that utilising the accepted method of purification the presence of percentages of carbon monoxide amounting to 0·0124 may be indicated, which amount may not actually be present in the air under examination

This objectionable compound may be removed by an absorbent of the type of animal charcoal inserted at the end of the purifying train, but in order to avoid any possibility of exhaustion of the absorbent unknown to the operator, it appeared advisable to remove entirely any possibility of any error due to the action of bromine.

Ten per cent fuming sulphuric acid was adopted as the most convenient absorbent for unsaturated hydrocarbons, etc Exhaustive tests indicate that this reagent is efficient, and provided the gas is slowly bubbled through a solution of potassium hydroxide after exposure to the sulphuric acid no indications of any abnormal action upon the iodine pentoxide have been observed.

There remains the third method under (*c*), page 3, to be considered, in which the carbon monoxide may be present in comparatively small quantities or in very small amounts, or may be varying—and the accurate determination is required over an extended period.

Under these circumstances it may be necessary to deal with comparatively large volumes of air; in particular when



[Fig. II.]

the percentage of contamination is varying, and an average sample is essential.

The method described below (Sinnatt *Analyst.* April, 1913) has been used for the estimation of carbon monoxide in waste gases from gas-heated irons and the exhaust gases from a gas engine.

The process involves the utilisation of iodine pentoxide as a reagent under conditions similar to those described on page 16 The gases before passing into the reaction chamber are purified by the elimination of such acid gases as sulphur dioxide and sulphuretted hydrogen, and also from unsaturated hydrocarbons.

There are practical difficulties involved in the utilisation of the above reaction, especially if this lies in the direction of the estimation of the iodine produced. If any large percentage of carbon monoxide is present in the gas the resultant iodine is readily condensed in the leading tubes, and to complete the estimation this must be volatilised by a steam of warm pure air, this requiring time and involving inaccuracies Thus a single determination may take five or seven hours. Normal air may contain as much as 0·0014 per cent. of carbon monoxide, and air free from carbon monoxide is somewhat difficult to prepare

Hence a method has been evolved which depends upon the collection of all the carbon dioxide produced after the carbon monoxide has been oxidised with iodine pentoxide

The gas is collected in a dry flask which admits of the carbon dioxide present being determined by Pettenkofer's process.

After purification the gas is passed into the tube A shown in the diagram (Fig. II) The leading tube A is sealed to the wider tube filled with iodine pentoxide and glass wool throughout its length, this enabling the gas to pass upwards through the iodine pentoxide

The tube A is sealed to a small catch bulb C which contains mercury, and the gas in passing through the mercury is freed from iodine. The sampling apparatus D has been described (Sinnatt. *Analyst.* 1912. 37. 12) and is a means for filling an evacuated vessel with gas at any desired rate

The following is a method of conducting a determination·

The capacity of the vessel E and the apparatus D is ascertained. The vessel E is then dried and connected to D. The two vessels are then swept out with air from which the carbon dioxide has been removed; the taps F and G are then closed and the apparatus and flask evacuated by means of a water pump attached to the open tap G. The mercury is allowed to enter the main tube D and the final height of the mercury column read accurately.

From the knowledge of the original volume of E the volume of gas space available in the gas flask can now be calculated.

The iodine pentoxide tube is then heated to the required temperature and connected to the source of gas to be examined. This is then aspirated through the iodine pentoxide tube and the mercury wash bottle until both are filled with either the gas to be analysed or the oxidation products. This is only necessary at the beginning of each set of determinations.

The evacuation flask and apparatus D are then connected to the mercury washing vessel C. The mercury is allowed to flow from the bottom of tube D at a suitable rate, that is, so that the gas enters the flask E at a rate of about one litre per hour.

The experiment may be left without supervision until the whole of the mercury has run from the burette, but it is generally found more convenient to stop the experiment and read off the level of the mercury corrected for the pressure of the liquid in the washing bottles. The volume of gas which is passed into the gas vessel is thus readily calculated, whilst a slight diminished pressure still remains in the gas vessel.

The tap H is now closed and the flask disconnected from the apparatus. A measured excess of standard barium hydroxide is run into a small cup, which is sealed into the top of the stopper of the flask, and the solution allowed to enter the flask as rapidly as possible

After standing for some little time with occasional agitation the excess of barium hydroxide remaining in the flask is determined by titration with $\left(\frac{N}{20}\right)$ hydrochloric acid, using phenolphthalein as an indicator.

The volume of carbon dioxide found is a direct measure of the carbon monoxide in the volume of gas which has been drawn into the apparatus.

The method of oxidation of the carbon monoxide in the gas may, if necessary, be altered in that a heated glass tube containing copper oxide and maintained at a red heat may be substituted for the iodine pentoxide. This method yields results identical with those obtained using iodine pentoxide as the oxidising agent.

The following results are quoted in order to show the accuracy of the figure which may be secured :

Percentage of CO in Gas	Percentage of CO (Oxidising Agent I_2O_5).	Percentage of CO (Oxidising Agent Copper Oxide).
2·20	2·07	2·07
0·673	0·700	0·682
0·041	0·040	0·041
0·025	0·025	0·024

Although the apparatus may appear somewhat complicated, it is actually in manipulation simpler than that necessary in order to aspirate and measure a similar volume of gas with any degree of accuracy.

There is no interference in the measurement of the volume due to any constituents being soluble in the containing liquid. The experiments require little attention during the actual passage of the gas.

In order to carry out a series of experiments all that is necessary on the completion of one is to attach a fresh gas flask which has been separately evacuated, and make the necessary connections.

Any desired volume of gas can be drawn into the same flask, that is, the experiments may be discontinued for any desired period of time and the sampling proceeded with at any pre-determined point. It is essential, however, that some slight diminished pressure should be left in the flask at the end of the experiment.

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The following bulletins were recently issued, Paper Wrapper, 2/- net :—

XI. A Contribution to the study of the Stone Dusting of Mines, Part II; by F. S. Sinnatt, M.B.E., M.Sc. (Tech.), and A. McCulloch, A.I.C.

XII The Chemical Composition of Iron Pyrites from Coal; by F. S. Sinnatt, M.B.E., M.Sc. (Tech.), and N. Simpkin, M.Sc. (Tech.), A.I.C.

and the following are in preparation :—

The Control of Coal Washing; by F. S. Sinnatt and C. G. Wood

The Methods of Study of a Coal Seam; by F. S. Sinnatt.

Messrs. H. F. & G. Witherby will have pleasure in registering the names of those interested in forthcoming bulletins, and in notifying the issue of each as it occurs.

TRANSPARENT PREPARATIONS *of* COAL *for* MICROSCOPICAL INVESTIGATIONS

By J. LOMAX, F.G.S., A.L.S.

AND

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BULLETIN XIV

TRANSPARENT PREPARATIONS *of* COAL *for* MICROSCOPICAL INVESTIGATIONS

In an article in a recent issue of "Fuel in Science and Practice," a brief description was given of the method of preparing transparent sections of coal. In the present bulletin it is proposed to elaborate that article and add one or two diagrams which were not considered desirable in the above brief publication.

The practical application of the knowledge obtained by the examination of thin preparations of sections of materials, is becoming of increasing interest commercially, but in the case of coal the interpretation of the observations are of greater complexity than is associated with sections of rocks, etc. On this account the subject may be considered to be developing somewhat slowly, and, although the writers have been engaged upon the work for over twenty years, few other experimentors have entered the field of research up to the present.

The reason for the scanty attention paid to the subject may, perhaps, be found in the difficulty associated with the actual preparation of the transparent slices, and it is proposed to describe this phase of the work in the present bulletin.

The writers and their assistants are able to produce thin transparent preparations about 8 in. by 4 in. in size, and relatively large preparations from coal of a fragile nature

The technique required for these preparations is one which the writers have gradually developed, but associated with it is the necessity for considerable experience of the properties of different coals.

Literature of the Subject

D. White and R. Thiessen (The Origin of Coal, Bulletin 38. U.S. Bureau of Mines. 1913) were among the first to give details of the method of preparation of coal sections, but it would appear that Mr. E. T. Newton (assistant palæontologist to the Geological Survey) was preparing coal sections about fifty years ago. The method of White and Thiessen is of considerable interest and the following is an abstract taken from their paper on the Origin of Coal. The abstract is given in detail in order that a proper comparison may be possible with the method to be described in this bulletin. It will be noticed that the size of their preparations appears to be limited to surfaces of about ½ in. by 1 in.

Grinding of Large Sections (The Origin of Coal, Bulletin 38. U.S. Bureau of Mines. 1913)

"Even under the most favourable conditions, it is impossible to obtain sections of coal of any considerable size with microtome. Larger sections are extremely valuable in order to obtain a general idea of the components and to determine the relationship and proportions of various lenses, laminations, and sublaminations. On the other hand, it is highly valuable to obtain sections, that are in their original condition, unchanged by any chemical action, to be compared with sections cut on the microtome from the same sample, that have undergone a preliminary chemical treatment. Large sections are, furthermore, of value in getting a correct orientation of the smaller microtome sections. In any event, ground sections, when they can be obtained thin enough are of greater value than microtome-cut sections. For photography, in particular, they have been found far more desirable. Hence section grinding is justifiable, in spite of its slowness. It has not been found possible to grind sections from the lower grades of coal nor from the higher grades of coal that absorb water readily, although much time has been spent in the attempt. With proper facilities, however, this may be possible. With the higher grades, especially coal not subject to weathering or not absorbing water readily, sections can be ground to a fair degree of thinness. On account of the opaqueness of the material the sections have to be cut to a much greater thinness than is necessary in rock or fossil-wood sections made by the same methods; but this thin cutting becomes extremely difficult on account of the greater softness and friability of the material. Sections ground under the most favourable conditions to the greatest possible thinness are still too thick for very high magnification. Yet ground sections are far better than microtome sections of the same thinness

" Carefully selected blocks are first carefully oriented and cut down to the required size; in most cases 10 by 20 millimetres is a convenient size for the surface and 10 millimetres for the thickness of the block. The size of the section, of course, depends much on the purpose for which it is to be used. That surface from which the section is to be cut is ground to a plain surface and polished to such a fineness that abrasion marks are no longer discernible under the microscope with medium magnification. Various means may be resorted to for this end, but the best one has proved to be the use of a carborundum disk of the finest grade possible, revolving at a moderate speed. At first a gentle stream of water should play on the disk, but when the surface is reduced to a fair degree of smoothness the disk may be used completely dry, but then requires great care. If necessary, the surface may then be burnished with a delicate chamois skin stretched on a rotating disk. The finest emery or carborundum dust has been found absolutely useless for this process. Although rouge gives a fairly good polish, yet fine particles of the rouge remain in the surface of the sample, where they are objectionable.

"The polished surface is next cemented, preferably by means of Canada balsam of proper consistency, to a slide whose surface is a true plane. As thin coal sections cannot easily be transferred as is done with rock or fossil-wood sections, a slide on which a specimen is to remain should at once be selected for permanent use Natural paper-filtered Canada balsam has proved the best medium for fastening the block to the slide. The balsam should be hardened by being placed over a sand bath, or, better yet, on a triangular copper table 12 to 16 inches in length, with the gas flame under the smaller end and the vessel containing the balsam at a point where at first there is heat enough to drive off the volatile matter until the proper hardness is attained. The proper degree of hardness is not an easy matter to decide and must be learned from experience. Tentatively, this point is reached when a part of the balsam removed, as on a toothpick, and cooled has such a consistency that it cannot be indented with the thumb nail, but is not brittle enough to break easily. The correct degree of hardness of the Canada balsam is the most important point in this part of the process. When the correct consistency has once been reached the balsam is moved farther away from the flame to that point on the copper table where it will remain in the proper condition.

"The slide and the block must be warmed to the same temperature as that of the Canada balsam. A small drop of balsam is applied to the slide and preferably another is put on the block, care being taken to have the balsam free from bubbles; the block is then carefully pressed to the slide as closely as possible. After having cooled, the specimen is ready to be ground.

"The first part of the grinding is easily done on a lapidary's wheel with any proper abrasive, such as emery or carborundum dust. When close down to the slide the finest abrasive possible must be used. Then the lapidary's wheel and abrasive may best be replaced by a carborundum wheel such as is used for polishing, and on this ground down to the required thickness; it is best to use water constantly on the wheel, because if the wheel is used dry the balsam heats and the section buckles and blisters. This part of the operation should be done with the greatest care. If, after the section is thin enough, further polishing of the surface is desired, it may be done with the chamois skin, as before. It is possible to grind sections as thin as about 10 to 5 microns. For low or medium power microscopes 10 microns is thin enough, but for all high-power microscopic work 10 microns is altogether too thick.

"Finally after having been dried thoroughly in the air, the specimen is covered with a thin cover glass over Canada balsam in the usual way, and is then ready for use.

"In the last stage of the grinding it may sometimes be advisable to stop the wheel and do the grinding by hand, by rubbing back and forth. Or a fine-grained whetstone such as a yellow Belgian hone, may be preferable to the lapidary's wheel, especially when a particularly thin section is desired."

G. Hickling (A Contribution to the Micro-Petrology of Coal, Trans.Inst.Min Eng. Vol. LIII. Part 3. Page 137) exhibits certain examples of photographs of micro sections, most of the sections for which were prepared by the authors.

Of the other workers who have been engaged upon this subject attention may be called to the paper by A. L. Booth on " The Economic Selection of Coal " (Iron & Steel Inst. September 21st. 1920) in which the author describes methods of selecting coal by the information obtained from the examination of thin sections. Incidentally this author includes in his paper 16 sections of coal and described each of them. The system of cutting sections used by Mr. Booth was probably very similar to the methods which the author has been using for many years, in view of the fact that he had every opportunity of becoming acquainted with the authors' methods.

E. P. Rheim (Jour.Chem.Met.Min.Soc. S. Africa. 1922. XXII. pp. 117-1314) (18 figs.) describes the microscopical appearance of certain South African coals and states that the preparation and examination by means of the microscope of thin sections in a matter of some difficulty. He has, therefore, developed a method by which polished surfaces of coal may be examined by reflected light.

There appears to be no advantage gained by this latter method of treatment and the results are not so illuminating as those obtained by the examination of thin sections.

Attention may be called to the work recently published " Coal, Its Properties, Analysis, etc." by D. K. Moore (John Wyley & Sons) in which there is a careful description of methods of preparation of thin slices of coal and the interpretation of the results obtained by their examination.

There is no intention of suggesting that these methods are not suitable for certain purposes, and the following is a brief account of the methods given in the above book

The first method consists in treating the coal with some reagent, which will remove the main proportion of inorganic matter. The coal remaining is now treated with some softening agent. Reagents for this purpose are potassium or sodium hydroxide either in aqueous or in alcoholic solution.

Thiessen recommends the use of the alcoholic solution as it produces a shrinkage in the organic matter which counteracts the expansion due to the presence of the hydroxide.

Other softening agents have been recommended as a means of obtaining the coal in such a form that sections may be cut by means of microtome. As pointed out in the early part of this bulletin, Thiessen has abandoned the use of the microtome and adopted the method of grinding.

The disadvantages associated with the process in which the coal is treated with a reagent must be emphasised. It is clear that if the coal is treated with a reagent prior to the cutting of a thin section, certain constituents of it must have been eliminated.

Perhaps the chief advantage associated with an examination of thin sections of coal is that they provide a means by which a permanent photograph may be made of any special features of a specimen of coal. The removal of the inorganic constituents, of constituents soluble in caustic potash, alcohol, phenol, etc., reagents which have been adopted for the softening of the coal substance, makes the photographic record incomplete.

The microscopical appearance of the inorganic constituents forms one of the most important pieces of evidence provided by the microscopical examination and it is impossible to study the organic substance of the coal in its true perspective in the absence of the inorganic or other constituents. On this account it is not considered that the treatment of coal with a reagent prior to cutting of sections can be a correct method of procedure.

In this bulletin it is not proposed to enter into the interpretation of the constituents made visible by photomicrographs.

The structure of the constituents from which the coal was formed may frequently be identified, the form in which the pyrites occurs can also be recognized and speaking generally the microscopic examination of well prepared thin sections constitutes one of the most valuable means for the investigation of the structure of coal seams.

The preparation of transparent sections may be considered under the following headings:

1. The method of obtaining a sample.
2. The position at which the section should be obtained, whether on the face or the end of the coal.
3. The preparation of the mass of coal for cutting.
4. The mounting of the polished block of coal upon a glass slip.
5. Mounting the block of coal.
6. Manipulation and preparation of the transparent section.
7. Completion of the preparation of the section.

Method of Obtaining a Sample

It is the usual practice to obtain a pillar of coal representing the whole of the seam. Such pillars of coal divide themselves naturally into a series of horizons. Frequently the height at which these natural fractures occur is too great for a complete section to be practicable. In view of this it is usual in the absence of natural partings to divide each of the blocks into a number of artificial horizons, so that each transparent section is approximately 3 by 4 in. or 3 by 6 in. This, however, is not the limit of size as it is possible to cut slices as large as 4 by 8 in.

"Face" and "End" of Coal

It is necessary to describe clearly the direction from which the coal was obtained from the seam. In the majority of instances there are three distinct directions in which the lumps of coal may be split during working: along the bedding planes, which are parallel to the floor and the roof; along the cleavage planes, the direction of which is at right angles to the dip of the seam; and across the "end," which is nearly at right angles to the cleavage plane or "face."

The cleavage plane is usually most well defined when the seam dips at a steep angle, or when it has been under the influence of considerable earth-movement. Many of the cleavage faces are covered with a mineral deposit to which the name "ankerite" has been applied; this is calcium carbonate, in which a portion of the calcium has been replaced by some other metal. When the coal is being won, this deposit falls from the seam in large flakes, the coal usually breaking at one of the cleavage faces. At right angles to this plane is the "end" of the seam, where the coal breaks without assistance from a line of cleavage.

When the bedding planes or dip of a seam are nearly horizontal, slight difference will be noticed between the appearance of the face and the end. This difference is most pronounced with soft friable coals, in which planes are developed in the manner indicated in fig. 2. It is probable that most of the cleavage planes can be ascribed to the thrust and tilting of the strata owing to faulting, and in a minor degree to the construction or texture of the coal substance. Where tough bands or beds are present in the seam, the face is never so clearly defined as when the coal is soft or brittle.

It will be understood from this description that if a section of coal for examination under the microscope is required from a block which contains a large number of cleavage planes, greater difficulty than usual will be experienced in preparing a section from the "face," owing to flakes breaking away from the block of coal. If, however, the preparation of the block previous to cutting a section is confined to the "end," the difficulty arising from the coal breaking away largely disappears. For this reason, it is our usual practice to cut most of our slices from the end of the coal. If the coal has but few cleavage faces, and is consequently not liable to break into cubical fragments, there is but little difference in the manipulation required to prepare a section from the face or from the end.

Preparing Samples for Cutting

It is exceptional to find a coal that is strong enough and coherent enough in its natural state to withstand the mechanical manipulation, such as grinding and polishing, incidental to the production of thin slices. Most coals disintegrate under such treatment, and it is essential for the preparation of good sections that such disintegration should be prevented. After much experiment it has been found that treatment of the blocks of coal with a binding solution, made by dissolving bleached or pale shellac in methyl alcohol, keeps them in a form compact enough to withstand the subsequent grinding and polishing. The solution is made of varying concentration according to the type of coal under examination, and has been found to act not only as an efficient binder but as a preventive against absorption of moisture by the more porous parts of the coal substance. The manner of application of the binding solution is largely a matter of experience.

As illustrating the necessity for this cementing treatment, two photographs are reproduced (Plate I). Fig. 1 is a photograph of the broken surface of a soft friable coal; numerous fine joints can be distinguished crossing one another at acute angles. By the intersection of these joints small cubical pieces of coal are formed, the sides of which are slightly inclined from the perpendicular,

PLATE I.

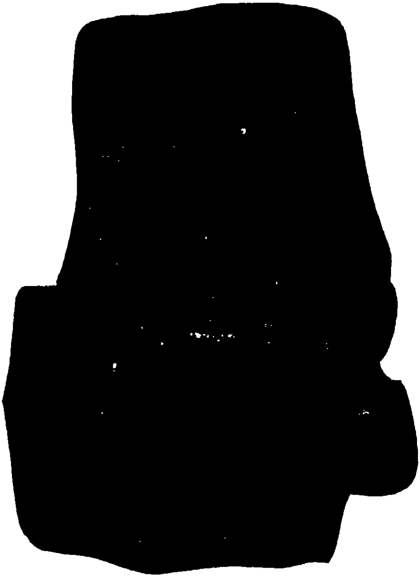
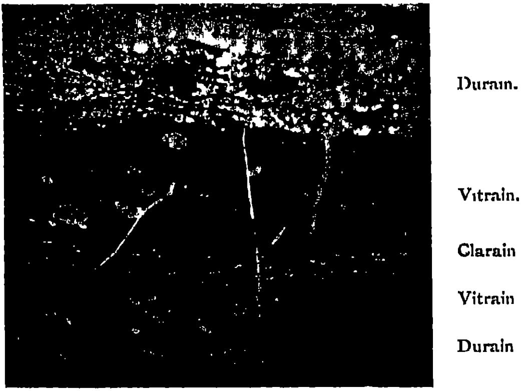


Fig. 1. BLOCK OF BANDED BITUMINOUS COAL



and are nearly parallel to the vertical faces of the seam; the other sides of the cubes are parallel to the bedding plane of the coal. Obviously, when attempting to grind and polish such a surface, it is almost impossible to ensure that all the small cubes of coal shall remain in their places; one may protrude above the surrounding surface and become torn off during polishing, thus loosening the whole of the coal adjacent to it.

Treatment of the coal with an alcoholic solution of shellac, however, produces within the interstitial spaces a thin adhesive layer which, when dry, binds the block into a coherent mass. Fig. 2 is a photo-micrograph from a preparation of the coal illustrated in fig 1. The cementing material is invisible, and it will be seen that all the particles of coal are held firmly in their proper positions. The introduction of the cementing material does not make any visible difference in the appearance of the section under the miscroscope, and does not therefore interfere with its examination.

Difficulties arising from the disintegration of the coal can thus be satisfactorily overcome. Another difficulty is caused by the presence of " occluded " gases. As is well known, most, if not all, coals contain within their substance gases which are slowly evolved at ordinary temperatures so soon as the coal is exposed to the air. They are supposed to be present either in solid solution in the coal substance or under high pressure within minute pores or interstices in the coal. At all events their rate of evolution is accelerated by heating the coal or by crushing it, and inasmuch as the operations necessary to prepare a coal section involve heating and crushing (*i.e.*, grinding) the coal, gases would be continuously evolved unless a preliminary treatment can remove them.

No doubt, if the coal were allowed to remain exposed to the air at ordinary temperatures during a sufficient length of time, the bulk of the "occluded" gases would depart; but is highly desirable that sections should be cut as soon as possible after the coal has been mined, lest changes, due to oxidation, for example, should occur in its characteristics. The evolution of gases, which would materially interfere with the preparation of good transparent sections, must therefore be countered; for, as will be described later, one stage of the preparation of a transparent section of coal involves the mounting of the block on a slip of glass, using as a mountant a material which at one stage of the proceedings is of the consistency of thin glue. If evolution of gases occurs after the block has been so mounted, and whilst the mountant is still viscous, innumerable small bubbles are produced between the slip of glass and the coal, and a satisfactory section cannot be produced. (See figs. 1 to 4, plate II.)

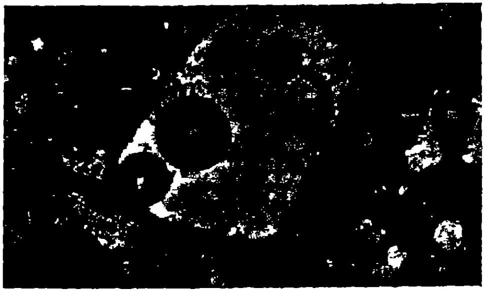
The question of air bubbles in the mounted preparations is of considerable importance and the illustrations in plate II (figs 1 and 2) are designed to exhibit the appearances of sections which have not been properly prepared.

Fig. 1 (magnification 25 diameters) shows a section cut from a block of coal in which no precautions have been taken in the preparation of the coal. In the field seven or eight gas bubbles may be seen. This gas has been evolved from the coal during the mounting, by the action of the heat necessary to liquefy the mounting reagents previous to the glass slip being pressed on to the surface of the section. It is noteworthy that the air bubbles are extremely prominent on the lighter backgrounds.

In fig. 2 (magnification 15 diameters) the block of coal had been only partially prepared before mounting, and in this case only a relatively few gas bubbles appear, whilst they are considerably smaller than those seen in fig. 1.

This photograph emphasizes one feature of the work, namely that not only is it important that the main volume

PLATE II.



ig 1. A horizontal section of coal with large gas-bubbles. Cut from a block without preparation

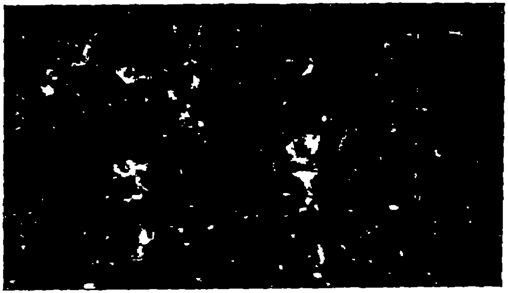


Fig 2. Vertical section of coal with small gas bubbles. Block partially prepared

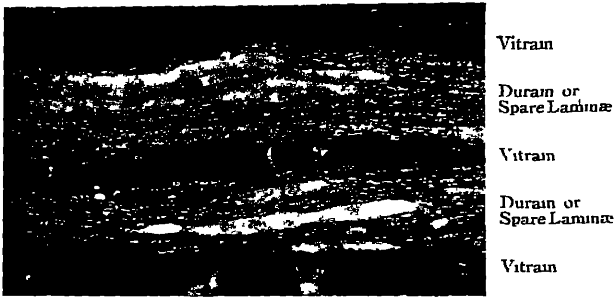


Fig 3. Vertical section Block perfectly prepared.

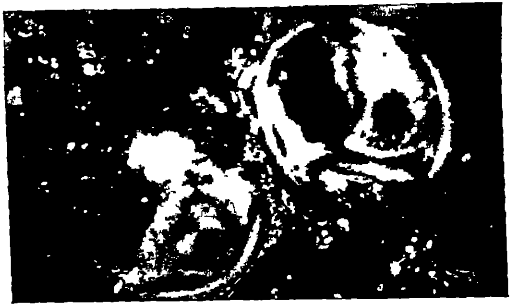


Fig 4 Horizontal section. Block perfectly prepared.

of gas should be removed, but that practically the whole of it should have been eliminated from the coal before the section is finally covered.

In figs. 3 and 4 (magnification 20 diameters) slices of coal cut from the same block are shown, all the precautions described in this bulletin having been observed.

The most satisfactory method of dealing with the evolution of gases is to maintain the block of coal from which the section is to be cut during several hours at a temperature a few degrees higher than that to which the coal is likely to be subjected throughout the remaining operations. This preliminary heating also serves to remove all moisture from the coal, the presence of which would militate against satisfactory results being obtained.

Briefly, then, the method of treating a block of coal, preparatory to mounting it upon glass, is as follows: When the block of coal has been cut to the required size it is immersed in a bath containing a soluton of pale shellac in methyl alcohol. The block should be completely immersed so that when it is removed the surface is covered with a thin film of shellac. The surface from which it is proposed to prepare a section is now cut and is then ground perfectly flat and smooth. This grinding removes the layer of shellac, exposing a fresh surface of coal, and it is therefore desirable during the grinding to employ as little water as possible lest the fresh coal surface should absorb it. After cleaning the coal free from grinding materials, etc., by washing it in a stream of water, it is dried in a water-jacketed oven at a temperature a little less than the boiling point of water, and is maintained at that temperature during four or five hours. At the end of this period the block is placed, with the freshly-ground surface downwards, in a shallow dish containing shellac solution, so that a layer of about ½ in. thickness of the coal is immersed; it is then maintained at a temperature rather lower than that used during the drying process, until the ground surface is saturated with shellac solution.

The next stage in the proceedings, after the block of coal has cooled, is to obtain as perfectly polished a surface as possible, level and free from scratches. The surface that was ground flat is rubbed upon a piece of plate glass, using carborundum powder as an abrasive; and the final polish is given with putty powder, using water as a lubricant. The surface is now ready for mounting on glass.

Mounting on Glass

After the block of coal from which it is desired to cut a section has undergone the preliminary treatment designed (*a*) to render it compact, and (*b*) to rid it of moisture and occluded gases, the next step is to mount the highly polished surface of the block on a slip of glass.

A considerable number of difficulties are associated with this stage of the process of section-cutting. They arise chiefly from the fragility of coal. As an adhesive for hard rock or mineral specimens solid Canada balsam is usually employed, but this mountant is unsuitable for the preparation of coal sections unless they are of quite small size. After a large number of experiments with various mixtures of balsams and resins, we have succeeded in obtaining a material which satisfies the requirements for large sections, namely, that it should be hard and tough, not readily scratched, and capable of adhering firmly to both coal and glass; it should also be colourless. Such a material is obtained by mixing specially selected pieces of copal gum, crushed to a fine powder, with liquid Canada balsam in the proportions of one to three.

The mixture is prepared by heating the two gums slowly over a sandbath until a cooled sample exhibits a sufficient degree of hardness. Care must be taken to avoid discoloration of the mixture during heating, by overheating, since in addition to being discoloured the mixture will then be brittle. The cooled mixture should be of such a degree of hardness that no impression is made on it when it is scratched with the finger nail.

The degree of hardness of the mixture can be modified, if required, by varying the proportions of the two gums. Thus, the hardness is increased by increasing the proportion of gum copal; this also raises the melting point of the mixture, so that a higher temperature would be required to cause the mountant to spread over the glass slip preparatory to attaching the specimen. It has been found that, in general, the best temperature at which to maintain the mounting medium lies between 110 and 115 deg. Cent.; but occasionally it may be desirable to go outside this range of temperatures, in which event the most suitable proportions of gums must be found that will yield a mixture of the right consistency at the mounting temperature employed.

The fact should be emphasised that in preparing coal-sections the block of coal itself should be subjected to as low a degree of heat as possible during mounting, for the reason already mentioned that occluded gases may be evolved which may form such a number of bubbles in the mounting medium, between the glass slip and the coal surface, as to destroy the value of the section when it is completed. When mounting specimens of rock for the cutting of sections, it is usual to heat the specimen so that the hot mounting medium may make good contact with the polished face. The absence of occluded gases from rocks in any but negligible quantities renders such heating of the specimen possible; and the heating is desirable, lest the contact between the face of the specimen and the glass slip hould be imperfect, for a cold surface placed in contact with the hot mounting medium cools the latter and causes a greyish, non-adhesive film to form between the two surfaces. During subsequent operations, for the production of a thin slice, the specimen would then peel off the glass.

Herein lies the difficulty so far as the production of sections of coal is concerned; it is desirable to heat the specimen so as to ensure proper adhesion of the mounting medium, and yet, in the majority of instances, it is imperative that the specimen should be mounted in the cold, lest occluded gases should be evolved. It was not until the mode of procedure now to be described was developed that this difficulty was overcome.

Heating the Glass Slips

With a view to obtain as great evenness as possible in the mounting of the blocks of coal, the method of heating the glass slips should be chosen with care. A satisfactory method is as follows: A cast iron plate, 12 in. square, is supported about 1 in. above the flame of a straight Fletcher burner, which is not placed centrally beneath the plate, but is nearer to one side. The glass slips covered with the mountant can then be heated to a higher temperature than is required to melt it, by placing them over the hotter parts of the plate, and then can afterwards be moved gradually towards the cooler part of the plate until the mountant cools to the proper consistency.

Mounting the Block of Coal

The temperature of the hot plate is raised to about 150 deg. Cent. (maximum), and a glass slip of either ground or polished glass, of the required size and thickness, is laid on the hottest part of it. A piece of the mounting medium is rubbed over the hot surface of the glass until it is covered with a layer about ⅛ in. thick. The glass slip is then drawn towards the cooler part of the plate. The block of coal on which the polished surface has been prepared in the manner already described, is polished with an exceedingly thin layer of shellac; then, just when the time for mounting it has arrived, the polished surface is covered with a thin film of oil of cloves, so as to form an amalgam between the mountant and block of coal.

When the glass slip coated with mountant has cooled to the right temperature, the polished surface of the block of coal is placed on it with an even pressure, expeditiously and yet without undue haste. On lifting the block of coal and examining the glass slip that is now adhering to it, a perfectly even black surface should be visible. If the surface appears uneven, or of light colour in patches, the coal must be pressed more firmly on the glass slip, which it may be necessary momentarily to heat again. This operation having been satisfactorily performed, the block of coal is placed, with the glass slip downwards, on a cold iron plate, which must be perfectly level. The transference to this cold plate should be made as quickly as possible after the attachment of the glass slip, so as rapidly to withdraw heat from the coal, which must be allowed to remain under pressure until the glass is quite cold.

Cutting the Section

When cutting thin slices of ordinary rocks, a disk of copper or soft iron is generally used, either charged with diamond dust or fed with carborundum or emery powder. In order that such a lapidary's cutting disk shall be efficient, the specimen to be cut must be harder than the material from which the disk is made, since its efficiency is dependent upon the pressing of the hard particles of the abrasive into the soft metal of the disk by the rock. When a sample of coal containing impurities, such as calcite, ironstone, or pyrites, is to be cut, the disk may be employed; but ordinarily coal is so soft and of such a comparatively spongy and cellular nature that the particles of abrasive are pressed into it by the comparatively hard metal of the disk.

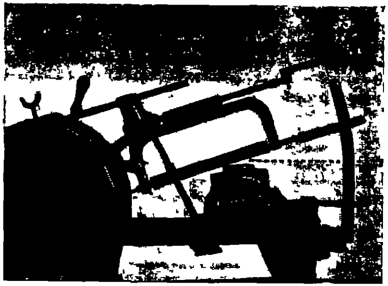
After many and long-continued experiments, I have come to the conclusion that the best method of cutting a thin slice from a block of coal is by means of a hack saw (see fig. 1, plate III), using blades about 1½ in. wide and 15 in. long, with 10 teeth to the inch I find it preferable to sharpen the blades myself and to leave the face of each tooth square. By having the teeth cut in this way, and not "set" in the usual manner, the cutting effect on the coal is produced during the forward stroke of the blade only and there is no dragging action on either side of the blade. By these means thin slices can be cut quite close to the glass slip, a thickness of ⅛ in. or less being usual (see fig. 2, plate III). As will be understood later, the thinner the slice that can be cut at this stage of the proceedings the greater will be the saving of time and labour during the more laborious operations of grinding the preparation to produce a transparency.

During the cutting of the section with a hacksaw the block of coal requires to be held firmly in some form of vice, the jaws of which should exert an even pressure over the whole surface.

The type of vice is shown in fig. 1 (plate III) It consists of a flat base board to which a rigid back is fixed at right angles: on the rigid back is an upright flange. A sliding block of wood is attached to the base board, the position of which can be altered by means of the small wheel shown in the picture. The whole is held in position by an ordinary vice.

The slice of coal may be cut to any desired thickness by adjusting the base board to the required position The block of coal, prepared as already described, and mounted on the glass slip, is placed in the vice with the glass in

PLATE III


Saw blade
Vice, rest and screws for regulating the pressure on block and thickness of slice when being cut.

ig 1. Hack saw machine for cutting thin slices of dry coal (1/20th actual size)

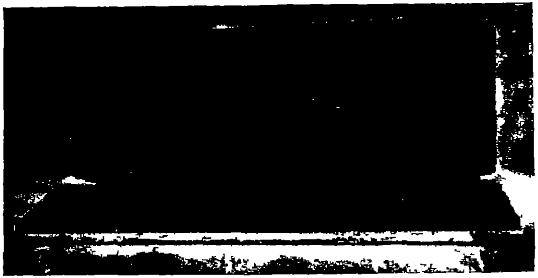


Fig 2 Block on glass slip, showing saw gap and partially cut to leave a slice on glass slip (¼ actual size)

Fig 3. Grinding laps and horizontal cutting discs

Fig 4. Large vertical cutting discs.

contact with the upright and rigid back. The front of the vice is now screwed until the wooden block is pressing against the surface of the coal.

The pressure exerted must be sufficient to secure the block of coal and prevent any movement during the backward stroke of the saw used for cutting the coal.

Fig. 2 shows a block of coal to which is attached a glass slip. The coal has been partially cut through and the position of the saw cut may be seen. The method of reducing the thickness of the slice of coal and removing the excess of coal substance is by means of a horizontally revolving lap which is illustrated in fig. 3.

Making the Transparency

When the thin slice of coal, adhering to the glass slip, has been prepared, the next process consists of reducing the thickness of the slice until it becomes transparent. Of all the methods of doing this that we have tried, the only one that can be regarded as satisfactory is that of grinding away the coal on a revolving cast iron disk or "lap," fed with carborundum powder (see fig. 3, plate III). A carborundum disk is not so efficient, since a hollow soon forms in the surface and sections of uneven thickness are thereby produced; with an iron lap this unevenness can be remedied by turning a fresh surface in the lathe. The lap we use is 12 in. in diameter and 1 in. in thickness, and is mounted on a vertical spindle so that the disk revolves in a horizontal plane within a shallow trough. Carborundum powder mixed with water is applied to the lap as it is revolving, and the coal section is held on the surface of the lap by hand.

Two or more laps are used with different grades of carborundum powder; the first, or coarse, grinding when the preparation is still fairly thick; the second, with a finer powder, when the section is comparatively thin; and the third, with still finer powder, when transparency is observable in parts of the section. Considerable skill and practice are required in the last stage of grinding on a lap; the least carelessness, or an ill-considered attempt to produce an especially thin section, may result in the whole of the slice being swept off the glass.

When the specimen has been ground to the minimum thickness that it is advisable to attempt to obtain on a revolving lap, further reduction of the thickness of the specimen must be carried out carefully by hand. At first this is done by rubbing the specimen on a thick glass plate covered with the finest carborundum powder, until portions of the edges of the film of coal begin to wear away altogether; when this occurs, carborundum powder should no longer be employed, but other means of reducing the thickness of the transparency must be sought.

By this time the specimen should have begun to exhibit distinctly the various bands and laminæ in the coal, but the major portion of the constituents will still be too opaque for examination under the microscope. It is necessary, therefore, carefully to reduce the thickness of each portion of the section until the whole of it is translucent. This is done by mounting the glass slip to which the coal section is attached on a retouching desk, such as is used by photographers, and grinding away the surface of successive portions of the section with stones similar to oilstones. Stones of different shapes and sizes are required according to the character of the bands in the preparation. Especial care must be taken when dealing with hard bands (e g., durain bands) that are lying between bands of softer coal; such hard bands must be worked upon with a stone separately, without touching the softer material.

In general, soft coals, such as those containing a high percentage of "volatile matter," are sufficiently translucent when the preparation is about 1/1500 in. thick; whereas hard coals must be not much more than 1/2000 in. in thickness in order that their structure shall be visible. It will readily be understood that these last stages of the work are those requiring the greatest skill and experience on the part of the operator.

Finishing the Preparation

The completion of the preparation for preservation involves the smoothing away of any unevenness at the edges, the cutting of the glass slip to a standard size, and the covering of the surface of the coal with some medium that will protect it from the atmosphere.

We cut each slide to a uniform width of 3 in., and allow the length to vary according to the size of the block of coal from which the specimen was prepared. The edges of the glass slip are smoothed by grinding with a fine carborundum lap, and any superfluous adhesive material is removed with a sharp wood chisel. The preparation is then thoroughly washed with soap and water and dried.

The best way to preserve the surface of the coal is to attach a thin cover glass to it. The largest preparations require a glass of No. 3 thickness, whilst for quite small specimens No. 1 thickness can be used. The cover glass should be cut to the required size and attached to the coal-section in the following manner.

Hard Canada balsam is heated with a small quantity of benzene until it reaches a temperature of about 110 deg. Cent., when it is a thin fluid. We now take the coal-section, which should be smeared over with oil of cloves, in order that the prepared balsam will readily flow over its surface, and pour sufficient of the balsam to form a thin film on its surface. The previously warmed cover glass is then put on the thin film of balsam, pressed firmly and uniformly upon the coal section, all excess of balsam being carefully squeezed out. Any superfluous balsam can be removed from around the edges of the cover glass with a heated knife, and the last traces can be cleaned away with benzene.

From the above description it will be gathered that owing to the opaque nature of coal the sections must be much thinner than ordinary specimens of rock and that the technique employed for coal sections is of an entirely different order from that used for rock sections. According to Hickling (vide ante) the thickness of coal sections would appear to vary from five to as little as one thousandth of a millimetre, whilst ordinary rock sections vary between thirty and forty thousandths of a millimetre. The excessive thinness required for coal sections is one of the reasons why thin slices are so difficult to prepare. A brief comparison of the method described above and that by White, Thiessen and Moore appears to indicate that it is necessary for the coal to be maintained in a compact form by means of a suitable medium, that the specimens should, as far as possible, be cut in a particular manner for certain types of coal, but that as a rule sections are best obtained from the end of the coal The suggestion that the sections may be cut by means of a microtome may now be dismissed as not being practicable. It is clear that the main essentials demanded from a transparent preparation of coal is that of uniformity and that uniformity of thickness may not be such an essential as uniformity of opacity. It is also clear from examples given above that the constituents of banded bituminous coal must attain a critical thinness in order that their various characteristics should be identifiable during a microscopical examination This latter part of the work, namely the reduction of the different parts of the section to the thickness which may be described as characteristic of the specimens, can only be carried on by one experienced in the preparation of such sections.

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